ODOUR AND GREENHOUSE GAS EMISSIONS FROM MANURE SPREADING

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Abstract

The Canadian livestock industry generates 150 million tonnes of manure annually and the majority of this manure is land applied. This practice allows the manure nutrients to be recycled to the soil crop system while improving soil fertility. However, land application of manure has the potential to negatively impact soil, water, and air quality if not managed properly. Microbial processes transform the manure nutrients into forms that are susceptible to leaching or volatilization. Balancing the nutrient loss dynamics from fertilized soil is very difficult because the nutrient transformations are affected by the soil environment such as air and water content, pH, and labile carbon content. All of these soil environmental factors can be influenced by manure application practices such as application rate, timing, and manure placement. Knowledge of how these management practices affect the soil environment can help producers make management decisions that reduce the likelihood of soil, water, and air contamination from manure application.

Very few data exist on how manure application practices affect odour emissions after spreading. Therefore, the efficiency of subsurface application in reducing odours from manure spreading for both solid and liquid manure was assessed. Flux chambers and dynamic dilution olfactometry were used to measure odour emissions from five livestock manure species applied at three application rates using surface and subsurface application methods. The results indicated that odour concentrations from injected plots were up to 66% (37% on average) lower than concentrations from broadcast applications. Injection seemed to have a larger impact on reducing odours from solid manure than liquid manure, mainly due to efficient manure coverage from solid manure injection. Odours measured immediately after solid manure applications were also 37% lower than from liquid manure applications. In general, odours from both manure types increased with higher application rates, but there was little difference in the odours among low, mid, and high application rates. The specific odour rate (odour emission rate per kg N applied) decreased with application rate due to the reduced surface area available for volatilization of compounds with higher application rates. Based on these results, injection of manure is an effective way to reduce the odour emissions immediately after spreading, particularly

for solid manure. However, other factors associated with manure injection, such as the increased power requirement and soil disturbance must be considered when evaluating the overall impact of manure injection versus surface application.

The odour data collected in this study described how management practices affected odours immediately after spreading. Knowledge of how these practices affect the emission rate trend over time is required to apply dispersion models to optimize the minimum separation distances for manure spreading activities. The model parameters for an existing volatilization model were determined from field and literature data and the resulting model allowed the effects of application mode (surface vs. subsurface) and manure type (liquid vs. solid) on odour emissions for 48 hours after application to be simulated. The effects of injection depth and a coverage factor on emissions were also simulated. The modeled peak fluxes from liquid manure applications were higher than those for solid manure applications, but the extended duration of odour emissions from solid manure resulted in higher cumulative losses from solid manure applications. While the application rate had no effect on the initial odour flux, higher application rates resulted in higher peak fluxes, higher overall emissions, and longer odour durations for both manure types and application methods. Modest injection depths were shown to reduce odours from both liquid and solid manure applications compared to surface spreading. The percent reductions in cumulative odours due to injection were estimated assuming typical coverage factors. The general predictions of the model developed in this study agree reasonably well with odour emission rate trends reported in literature. Future work should focus on better estimation of the model parameters and the variation of effective diffusivity with time and soil conditions.

Greenhouse gas (GHG) emissions from agricultural activities such as land application of livestock manure cannot be ignored when assessing overall emissions from anthropogenic sources. Like odour emissions, the magnitude of the GHG emissions will be influenced by management practices such as manure placement during land application. The GHG fluxes resulting from the surface and subsurface application of liquid and solid manure were also compared within 24 hours of application using a static

chamber and gas chromatography. The results showed that carbon dioxide equivalent (CO_2-e) fluxes were approximately three times higher from the injected plots than the surface plots for both solid and liquid manure. The elevated CO_2-e fluxes were mainly due to a pronounced increase in N_2O fluxes which was likely caused by increased denitrification rates. The CO_2-e fluxes from the liquid manure applications were also approximately three times higher than the CO_2-e fluxes from the solid manure applications, probably due to higher levels of ammonium available for nitrification and subsequent denitrification. The CH_4 fluxes were generally low and the treatments had no effect. The measured specific fluxes (total flux per kg N applied) remained relatively constant with application rate, indicating that, in this study, GHG emissions from manure applications were approximately proportional to the amount of land applied manure.

While the data from this study showed that manure type and placement influenced short-term nitrous oxide (N_2O) emissions, manure management practices (particularly slurry injection or solid manure incorporation) have the potential to influence long-term emissions by changing the magnitude and pattern of the nitrogen cycle in the soil-plant system. Management practices also impact the magnitude of other nitrogen losses (ammonia volatilization, nitrate leaching) which affect indirect N_2O emissions. A model that simulates the environmental conditions and nutrient transformations after manure application may allow a more reliable prediction of the effect of management practices on total GHG emissions. Numerous process-based models have been used to estimate N_2O emissions as influenced by agricultural practices in Canada. However, these models do not account for enhanced denitrification that potentially exists after slurry injection or manure incorporation, resulting in an underestimation of N_2O emissions. A simple mass balance of nitrogen after application to land showed that enhanced denitrification can increase total N_2O-N emissions by a factor of 5. By accounting for the increased microbial activity, slower oxygen diffusion and higher water filled pore space that exists after manure injection, models may better estimate N_2O emissions from manure application practices.

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List of Symbols and Abbreviations

1X, 2X, 3X, 4X	One year, two year, three year, and four year application rates (Mg/ha or m^3/ha)
A	Cross sectional area of chamber (m^2)
A_c	Cross sectional area of main chamber of wind tunnel (m^2)
ANOVA	Analysis of variance
A_s	Total surface area covered by wind tunnel (m^2)
ASTM	American Society for Testing and Materials
C	Carbon
C_0	Concentration of sub-sample drawn at time = 0 (ppm)
C_1	Concentration of sub-sample drawn at time = t_1 (ppm)
C_2	Concentration of sub-sample drawn at time = t_2 (ppm)
C_{amb}	Gas concentration of ambient air (ppm)
CF	Coverage factor (%)
cfm	Cubic feet per minute
C_G	Concentration of contaminant in vapour phase (g/m^3 of soil air)
CH_4	Methane
C_L	Concentration of contaminant in liquid phase (g/m^3 of soil solution)
C_o	Initial odour concentration (OU/m^3)
CO_2	Carbon dioxide
CO_2-C	Carbon dioxide carbon (12/44*CO_2)
CO_2-e	Carbon dioxide equivalent
C_{samp}	Gas concentration of sampled air (ppm)
C_T	Mass of solute per soil volume (g/m^3)
d	Thickness of stagnant air boundary layer (mm)
d.b.	Dry basis
D_E	Effective diffusion coefficient or effective diffusivity (m^2/day)
D_G	Gaseous diffusion coefficient (m^2/day)
D_g^a	Diffusivity of gas in air (m^2/day)
D_L	Liquid diffusion coefficient (m^2/day)
D_l^w	Diffusivity of gas in water (m^2/day)
DNDC	DeNitrification DeComposition model
E	Odour emission rate or flux (OU/m^2-s)
EF	Emission factor
EFEM	Economic Farm Emission Model
F or f_o	Surface gas flux (mg/m^2-s)
f_{oc}	Organic carbon content (decimal)
FYM	Farmyard manure
GC	Gas chromatography
GC/FID	Gas chromatography/flame ionization detection
GC/MSD	Gas chromatography/mass spectroscopy
GHG	Greenhouse gas
H	Hydrogen
H_2O	Water

H_E	Boundary transfer coefficient (m/s)
HIP	Hole in pipe model
IFSM	Integrated Farm System Management
IPCC	Intergovernmental Panel on Climate Change
J_s	Solute mass flux (g/m^2-s) or odour flux (OU/m^2-s)
J_w	Liquid water flux (g/m^2-s)
K	Potassium
k	Experimental constant for micrometeorological technique (dimensionless)
K_H	Henry's constant (Pa-m^3/mol or dimensionless)
K_m	Michaelis-Menten parameter representing time at which loss reaches half of maximum
K_{oc}	Organic carbon partition coefficient (m^3/kg)
L	Thickness of covering layer (m)
N	Nitrogen
n	Number of samples
N(t)	Cumulative loss at time t (kg/ha)
N_2	Nitrogen gas
N_2O	Nitrous oxide
N_2O-N	Nitrous oxide nitrogen (28/44*N_2O)
NH_3	Ammonia
NH_3-N	Ammonia nitrogen (14/17*NH_3)
NH_4^+	Ammonium
NH_4-N	Ammonium nitrogen (14/18*NH_4)
N_{max}	Michaelis-Menten parameter representing total loss
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NO_3	Nitrate
NO_3-N	Nitrate nitrogen (14/62*NO_3)
N-tot	Total N (kg/Mg or kg/m^3)
O_2	Oxygen
OC	Odour concentration of sample (OU/m^3)
OU	Odour unit
P	Phosphorus
PAMI	Prairie Agricultural Machinery Institute
ppm	Parts per million (by mass unless otherwise specified)
PVC	Polyvinyl chloride
Q	Flow rate of sweep air in chamber (m^3/s)
R^2	Coefficient of determination (dimensionless)
RH	Relative humidity (decimal or %)
S	Sulphur
SOC	Soil organic carbon
SRC	Saskatchewan Research Council
t	Time or time interval (s, min, hr, day as specified)
$T_{1/2}$	Half life of compound (day)
TAN	Total ammoniacal nitrogen
u	Wind speed for micrometeorological technique (m/s)
U of S	University of Saskatchewan

V	Velocity of air in wind tunnel (m/s)
V_E	Effective solute convection velocity (m/s)
VOC	Volatile organic compound
vs.	Versus
W	Thickness of contaminated material (m)
WFPS	Water filled pore space
Z	Soil depth (m)
$\Delta C/\Delta t$	Rate of change of gas concentration in chamber headspace (ppm/s)
ε	Total porosity (decimal)
ε_a	Air filled porosity (decimal)
θ	Volumetric moisture content (decimal)
ρ or ρ_b	Density of measured gas or soil (kg/m^3)
μ	First order degradation rate of compound (day^{-1})

Chapter 1

1.0 Introduction and Objectives

The agriculture and agri-food system is a substantial contributor to the Canadian economy, adding 8% to Canada's gross domestic product (GDP) in 2005 (AAFC, 2008). Livestock production (including red meats, dairy and poultry) account for almost half of agriculture's farm cash receipts. In 1996, livestock contributed 7.6 billion dollars to Canada's economy (CFA, 2007). Livestock production is, therefore, a major component of the agricultural sector and Canada's economy.

The largest by-product of livestock production is manure. Approximately 150 million tonnes of manure are produced and handled each year in Canada (Statistics Canada, 2006). The most common method of manure disposal is to apply it to the land. If applied in a timely fashion, manure is a valuable source of important plant nutrients such as nitrogen, phosphorus and potassium. In addition to offsetting the cost of commercial nitrogen fertilizer, adding manure to soil improves soil tilth, organic matter content, and water holding capacity. When applying manure to land, producers must ensure maximum utilization of the manure nutrients by crops while minimizing the negative environmental impacts. Without this proper balance, the disposal of livestock waste can be costly and negatively impact the soil, water, and air surrounding the application site.

Land application of manure results in complex biological and chemical interactions within the soil, water, and air. While application of manure offers several benefits to the soil, poor management practices can result in nutrient, pathogen, and heavy metal build-up in the topsoil, reducing the soil's capacity to support healthy plant growth. Applying

manure or slurries to land can also lead to groundwater contamination by nitrate after nitrification of the ammonium nitrogen present in the manure. Excessive application rates, application on slopes, or application near bodies of water can lead to surface runoff and eutrophication of sloughs and creeks through phosphorus and nitrogen movement with the water. Finally, manure spreading contributes to a large portion of the livestock industry's odour and greenhouse gas emissions. Although nitrate leaching has received much attention as an economic loss, a cause of eutrophication and a health hazard, gaseous emissions may eventually prove to be the most serious environmental concern (Jenkinson, 2001). Concerns about clean air and water have resulted in opposition to both existing and proposed animal operations (Bickert, 2003).

Livestock odours are a nuisance to neighbours and a potential health hazard to farmers and the community. The negative public perception can also restrict the sustainable expansion of the industry since communities are often opposed to intensive livestock facility development. Therefore, recent research efforts have examined technologies and practices to reduce odour emissions from the production buildings, manure storages, and manure spreading. Various studies have shown that the best way of reducing ammonia volatilization and odour emissions from slurry application is to reduce the air contact of the slurry by incorporation or injection into the soil. However, the efficiency of sub-surface application in reducing odours from solid manure application has not been previously investigated. Since almost two-thirds of the land receiving manure in Canada is applied with solid manure, practices to reduce ammonia volatilization and odour emissions from solid manure spreading need to be investigated.

In addition to the issue of odours from manure spreading, greenhouse gas (GHG) emissions from organic fertilizer management and application are also a concern. Up to 10% of the global emissions of 16.2 Tg/year of nitrous oxide nitrogen (N_2O-N) are reported to come from the nitrous oxide emitted after fertilizer and manure applications (Mosier et al., 1996). Statistics Canada (2006) reported that 36 million hectares of land were cropped in 2005 with 25 million hectares receiving commercial fertilizer and 3.4 million hectares receiving manure. A further 10 to 30% of the global emissions of N_2O-N

comes from the nitrous oxide (N_2O) emitted from non-agricultural soils (Jenkinson, 2001; Van Groenigen, 2004). Cole et al. (1997) suggested that with better application timing and management, N_2O emissions from manure spreading can be reduced by 50%. Because of the magnitude of agricultural N_2O emissions and the potential of carbon credit trading, greenhouse gas reducing technologies are an attractive option for livestock producers. Injection or incorporation of manure into the soil may reduce odour emissions, but sub-surface application of fertilizers has the potential to affect the GHG emissions after manure application. With new plans and strategies being put in place to reduce global GHG emissions, it is important to carefully analyze emissions that result from all technologies and practices.

Even though there has been much recent research on gaseous emissions from agricultural soils, methods of emission measurement are not perfect. The main reason for this is that GHG emissions are highly variable in time and space, requiring a high number of repetitions from labour-intensive chambers or complex and costly micro-meteorological equipment. Similarly, odours are composed of more than 200 volatile organic compounds which are sensitive to sampling equipment and techniques. Since gaseous emissions are highly dependent on the environmental conditions at the time of collection, sampling protocols can also significantly affect the results. In order to improve the reliability of the measurements and results, proper sampling equipment and protocols must be used when assessing GHG and odour emissions from agricultural soils.

The objective of this work is to provide a scientific comparison of greenhouse gas and odour emissions immediately after the application of solid and liquid manure using surface and sub-surface application methods. Mechanistic models are developed to describe the patterns in odour emissions over time after application. Existing GHG emission models are examined and modifications are suggested to improve their estimates and account for the effects of subsurface application. These models will assist in predicting the dispersion of odours surrounding application sites and add to our understanding of the contribution of manure spreading to national GHG emissions. The data will allow the emission reduction potential of land application technologies to be

evaluated and may be used as a benchmark for agricultural carbon credit trading. If the greenhouse gas and odour emissions and dispersion surrounding livestock operations can be reliably predicted, better decisions on siting can be made so as to not cause nuisance or health threats to neighbours while maximizing land-use efficiency and lowering the livestock industry's contribution to agricultural GHG emissions.

The specific objectives of this work include:

- evaluating existing equipment and protocols for emission determination following land application of manures and, if required, developing new protocols and equipment for sample collection,
- evaluating the relative odour and GHG emissions from various types of solid and liquid manure with both surface and sub-surface application,
- developing and validating a mechanistic model for the prediction of the odour emission rates following land application of liquid and solid manure, and
- reviewing the suitability of existing GHG emission models for the prediction of emissions following surface and subsurface application of manure.

This thesis is organized into five independent papers. Chapter 2 outlines manure application practices and associated environmental considerations. Chapter 3 reports on the assessment of odour emissions measured from manure spreading trials while Chapter 4 covers GHG emissions from manure spreading trials in Saskatchewan. The development of a mechanistic model to predict the odour emission rate trend over time after application is covered in Chapter 5 and Chapter 6 includes the GHG emission model review. Finally, Chapter 7 presents the general conclusions and recommendations drawn from this work.

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Chapter 2

2.0 The Environmental Impact of Manure Spreading

When properly managed, land application of manure is an environmentally responsible way to recycle manure nutrients and improve soil quality. Organic fertilizers have several benefits over synthetic fertilizers, including increasing the organic matter content and microbial activity in the soil and maintaining the soil's ability to recycle nutrients. However, poor management practices have the potential to negatively influence the soil, water and air quality surrounding application sites. Over-application can result in nutrient and heavy metal build up in the soil or nutrient contamination of surface and ground water sources. The timing of manure application can also promote leachate losses as well as transformations that lead to gaseous losses of nitrogen compounds. Manure placement can enhance nutrient transformations such as denitrification by placing the nitrate and carbon rich material in partially anaerobic conditions. Enhanced denitrification may result in higher emissions of nitrous oxide. All manure management activities such as manure storage and land application have the potential to impact the microbial environment in the soil which affects the transformations of the nutrients in the manure and soil. Specific forms of nitrogen such as nitrate and ammonia are more susceptible to leaching or volatilization, increasing the risk of environmental contamination. Proper management of these manure management activities can minimize the risk and promote manure application as an environmentally sustainable practice.

2.1 Introduction

Manure has been used for centuries as a fertilizer for crops and a conditioner for soil. In the early 1900's, animal manures were viewed as a valuable by-product from livestock production since application to the land provided nutrients for the soil and crop and improved the soil tilth by increasing the organic matter content, reducing bulk density and improving water holding capacity. However, estimating nutrient application when spreading manure was a difficult task, so when mineral fertilizers were introduced during the 1940's, farmers preferred this convenient and inexpensive alternative to animal manure. Animal manure, once viewed as an important soil conditioner and a source of crop nutrients, began to be viewed as a waste and potential pollutant (Bickert, 2003). Recently, environmental concerns, high nitrogen prices, the desire to improve topsoil conditions, and improvements to manure handling equipment have brought manure application back to the forefront as a viable alternative to synthetic fertilizer use. In order to minimize the adverse environmental impacts of manure application, management practices must consider proper methods of application and application rates.

The challenge with treating manure as a fertilizer is its heterogeneous nature. Additionally, the relative concentration of the inorganic nutrients in livestock manure is much lower than commercial fertilizers, resulting in larger quantities being required for soil-crop systems (Laguë et al, 2005). Handling large quantities of non-homogenous material can be quite challenging and costly. Because livestock manure contains both inorganic and organic forms of nitrogen, utilization and losses after land application are more complex than for synthetic fertilizers (Laguë et al., 2005). Furthermore, the nutrients in manure are usually not proportional to the nutrient requirements of the soil and the nutrient content of manure can vary between sources (Schoenau and Assefa, 2004; Laguë et al., 2005; Schoenau, 2006). Uniform application can be a challenge because of manure's heterogeneity, often resulting in over and under application of nutrients in the same field. Uniform application of liquid manure is generally easier to achieve than uniform application of solid manure due to the ability to pump and meter

liquid manure. Improved handling and distribution uniformity of solid manure was discussed in Laguë et al. (2006).

Manure is handled and applied in the form in which it exists on the farm. Solid, semi-solid or liquid manures are common, depending on the manure management system and type of animal. The total area in Canada applied with solid manure is twice as high as the total area applied with liquid manure (Statistics Canada, 2006, refer to Table 1.1). Generally, liquid manures can be applied quite evenly and with more control over the application rate due to its ability to be pumped and metered. Liquid manure can be applied using all of four techniques (broadcast surface application, banded surface application, direct injection and incorporation (Laguë et al., 2005)), but solid manure application is currently limited to broadcast surface application and incorporation. Recent work has resulted in manure prototype applicators to band apply and inject solid and semi-solid manure (Khalilian et al., 2002; Glancey and Adams, 1996; Laguë et al., 2008). Since solid manure application is common in Canada, environmentally sustainable methods of solid manure application are required.

Choosing an application rate is a balancing act between time and energy efficiency and applying the appropriate amount of nutrients. Application rates should be based on the nutrient requirements of soil (considering residual nutrients, expected yield of crop, previous applications of manure, crop residues, etc), the nutrient content of the manure, and the application method. Typical crops grown in the prairies require between 50 and 100 kg N per hectare for optimum growth, with lesser and varying amounts of other nutrients such as phosphorus (P), potassium (K) and sulphur (S). To reduce time spent in the field and soil compaction effects, farmers may apply high rates of manure once every two or three years rather than low rates once every year. While this is a common practice in the Canadian Prairies, repeated excessive application rates can exceed the nutrient requirements of the soil by two to three times in the application year, increasing the risk of contamination of the receiving environment (Schoenau and Davis, 2006).

Even with these economic limitations and physical challenges, manure application to land is a very common practice. Virtually all of the 150 million tonnes of manure produced annually in Canada were applied to 3.5 million hectares of land in 2005 (Statistics Canada, 2006). Relatively small amounts of manure are used for energy production (i.e. biogas from anaerobic digesters), but even anaerobic digesters produce a sludge waste that is often land applied. A summary of the area applied with manure and the types of manure applied in Canada and Saskatchewan is presented in Table 2.1. While 3.4 million hectares of land received manure N, just over 25 million hectares received commercial fertilizer (Statistics Canada, 2006). Hutchinson et al. (2007) reported that commercial fertilizer application represented 1.6 million tonnes of N input per year while animal manure application represented 375,000 tonnes of N input per year.

Table 2.1. Summary of land area applied with manure in Canada and Saskatchewan (Source: Statistics Canada, 2006).

	Area applied in Canada (ha)	**Area applied in SK (ha)**
Composted manure[1] (incorporated)	466,744	83,036
Composted manure (not incorporated)	223,777	32,330
Solid manure (incorporated)[2]	948,047	163,905
Solid manure (not incorporated)	656,370	83,097
Liquid manure (injected)	617,687	38,894
Liquid manure (surface)	465,373	6,161
Liquid manure (irrigated)	21,484	919
Total	**3,399,482**	**408,342**
Total solid	2,294,938 (67.5%)	362,368 (88.7%)
Total liquid	1,104,544 (32.5%)	45,974 (11.3%)
Total surface applied	1,367,004 (40.2%)	122,507 (30%)
Total sub-surface applied[3]	2,032,478 (59.8%)	285,835 (70%)

[1] "Composted" manure presumably refers to stockpiled solid manure from pen clean outs.
[2] Solid manure incorporated: majority was incorporated more than 7 days after application (i.e. during seeding or seed preparation).
[3] Total sub-surface applied includes incorporated solid manure and injected liquid manure.

The vast area to which manure is applied every year means there is a high risk of extensive environmental damage if the manure is not applied properly. This paper discusses manure application practices such as timing, rates and modes of application and their impact on the soil, water and air surrounding the application site. Since the environmental impacts of manure application are highly dependent on nutrient dynamics, the microbial activity that drives nutrient transformations is discussed first.

2.2 Microbial activity and nutrient cycling

The impacts of manure application on soil, water and air quality are dictated by the nutrient transformations and nutrient movement that follow manure application to the soil. The majority of nutrient transformations in the soil are performed by the abundant microbial population. Microbes survive and gain energy by breaking the carbon bonds of dissolved organic compounds, transferring electrons in the process (Li, 2007). All nutrients required for plant and microbial growth (nitrogen, carbon, phosphorus, sulphur, etc.) are abundantly available in most manures and undergo complex transformations after application due to these electron transfers. Grant et al. (2006) summarized the important microbial transformations that occur in soil for the prediction of nitrous oxide (N_2O) emissions. These include:

- mineralization and immobilization of ammonium by numerous microbial populations,
- oxidation of dissolved organic carbon and reduction of oxygen by heterotrophs,
- oxidation of dissolved organic carbon and reduction of nitrate, nitrite and N_2O by denitrifiers,
- oxidation of ammonium and reduction of oxygen by nitrifiers,
- oxidation of nitrite and reduction of oxygen by nitrifiers,
- oxidation of ammonium and reduction of nitrite by nitrifiers,
- uptake of ammonium and reduction of oxygen by roots and mycorrhizae, and
- cation exchange and ion pairing of ammonium.

The basic transformations of nitrogen and carbon are most important when examining the environmental impacts of manure application and are discussed further.

2.2.1 Nitrogen Transformations

The nitrogen cycle in Figure 2.1 illustrates the complexity of nitrogen transformations which involve different microbial populations for each stage. Chemical transformations

of nitrogen such as nitrification, denitrification, mineralization, and N-fixation are performed by a variety of soil-inhabiting organisms. Physical transformations of N include several gaseous forms which move freely between soil and the atmosphere.

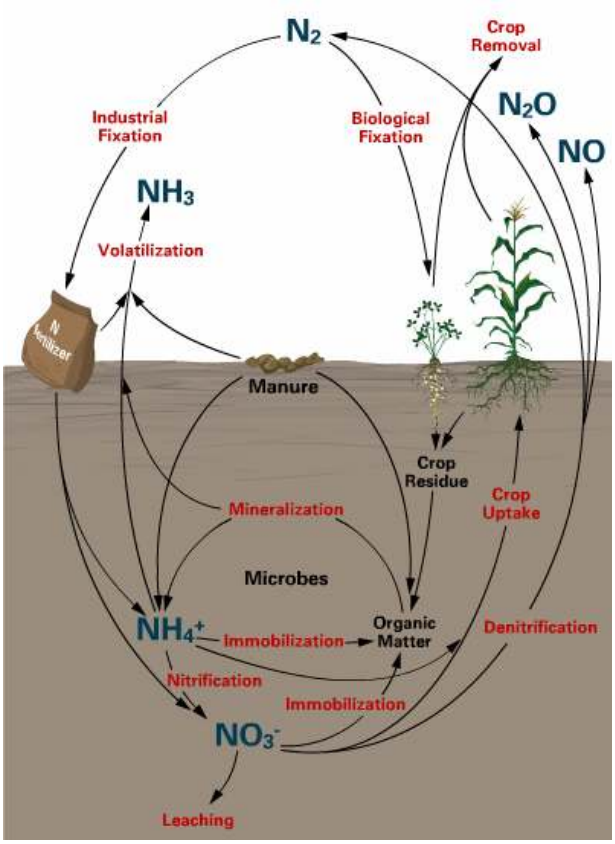

Figure 2.1. The nitrogen cycle. (Reproduced with permission from Johnson et al. 2005).

Although the nitrogen cycle has no "starting" point, nitrogen transformations can be examined by beginning with the application of organic and inorganic nitrogen (nitrate or ammonium) in the form of manure. After application to the soil, organic nitrogen is transformed to ammonium by soil microbes via mineralization, ammonium nitrogen is transformed to nitrite and nitrate by nitrification and some nitrate nitrogen is transformed to nitrogen gas by denitrification. Nitrous oxide is a by-product of both nitrification and denitrification (Watanabe et al., 1997).

Ammonium is the plant available form of nitrogen that is taken up and synthesized by plants. Nitrate can also be utilized by plants, but since nitrate is negatively charged, it is

repelled by the negatively charged soil particles. This means nitrate nitrogen is susceptible to leaching into the groundwater. Nitrate rich water is a danger to human and animal health because if it enters the bloodstream it can block the blood's ability to absorb oxygen. Another form of nitrogen, nitrous oxide, is recognized as a potent greenhouse gas with a global warming potential that is approximately 300 times higher than carbon dioxide over a 100 year time span (IPCC, 2007). Nitrous oxide is also known to react with stratospheric ozone and contributes to increased UV-B intensity at the earth's surface (Socolow, 1999 in: Hutchinson et al., 2007). Since nitrate and nitrous oxide are the environmentally hazardous forms of nitrogen, the processes that have the potential to negatively impact the environment after manure application are nitrification and denitrification.

Nitrification is the biological oxidation of ammonium to nitrate with nitrite as an intermediate (Bremner, 1997). Relatively small amounts of N_2O are a byproduct of the nitrification reaction (Schmid et al., 2001). Nitrous oxide production during nitrification is thought to be produced when the nitrifiers are under stress (Lemke et al., 2009). Autotrophic microbes are largely, if not entirely, responsible for nitrification in most soils (US EPA, 2002). Various groups of heterotrophic bacteria and fungi can also carry out nitrification, although at a slower rate than autotrophic organisms (US EPA, 2002). The most frequently identified genus of ammonia oxidizing bacteria includes *Nitrosomonas* while the nitrite oxidizing bacteria includes *Nitrobacter.* The first stage of nitrification requires oxygen to oxidize the ammonia molecules to nitrite (US EPA, 2002).

First stage of nitrification *(Nitrosomonas):*

$$NH_3 \text{ (or } NH_4^+) + 0_2 \rightarrow NO_2^- + 3H^+ + 2e^-$$

Second stage of nitrification *(Nitrobacter):*

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$

Nitrification may also lead to N_2O production during oxidation of NH_4^+, possibly as a response to NO_2^- accumulation (Anderson and Levine, 1986 in: Petersen, 1999).

The breakdown of dissolved organic carbon (DOC) requires the transfer of electrons from the DOC to an electron acceptor. Since oxygen has a low Gibbs free energy value, it is the first candidate as an electron acceptor (Li, 2007). In oxygen limiting environments, microbes with the alternative capacity to reduce N oxides will use the chemically available oxygen in surrounding nitrate as an electron acceptor to reduce nitrite and nitrate to nitrogen gas. This is known as denitrification.

Denitrification is the microbial reduction of nitrate successively to nitrite and then to the gases NO, N_2O and N_2 (NRCS, 2007). If the intermediate product N_2O is able to escape from the anaerobic microsites before it has been further reduced to dinitrogen, a net emission of N_2O will occur (Li, 2007). A wide range of heterotrophic bacteria and fungi are able to reduce NO_3 and NO_2 to N_2O or N_2 during denitrification under anaerobic conditions (Bateman and Baggs, 2005).

The key factors that drive nitrification and denitrification are soil pH, soil temperature, ammonium and nitrate concentrations, levels of oxygen, amount of organic matter available to the denitrifying bacteria, and labile carbon content (Bremner, 1997). Other factors include water holding capacity of soil, irrigation practices, fertilizer rate and type, tillage practice, soil type, vegetation, land use practices and use of chemicals (Freney, 1997). Hosen et al. (2000) also included factors such as soil aeration, soil water content, type of inorganic nitrogen (ammonium vs nitrate), soil types, soil texture, soil tillage, organic material availability, crops and vegetation, temperature and season. Basically, any factor that affects the amount of substrate available to microbes, their environment and ultimately their activity will influence nitrogen transformations. The factors that are most commonly affected by manure application practices are the oxygen and carbon contents of the manure and soil and the type of nitrogen available in the manure.

Nitrification and denitrification can occur simultaneously in soils, although the rate of the two processes depends strongly on the soil oxygen content and the availability of organic material that can be utilized by denitrifiers for reduction of nitrate. Early work surmised that all of the N_2O evolved from soils was produced through reduction of nitrate by

denitrifying microorganisms under anaerobic conditions (Meng et al., 2005). But now it is understood that nitrifying microbes also contribute to emissions of N_2O from soils. Even so, the majority of N_2O emissions from soils results from denitrification activity.

The level of oxygen where denitrifiers take over from nitrifiers in various soil types has been examined by studying the effect of water filled pore space (WFPS) on nitrification and denitrification activity. WFPS represents the ratio of total pore space filled by water and is used to compare oxygen content rather than moisture content since different soil textures will have different volumes of pore space available for water and air. The WFPS for a coarse soil can be directly compared to the WFPS of a fine soil.

At low WFPS (approximately 20%), microbial activity may be limited by substrate diffusion and water availability (Bateman and Baggs, 2005). However, as WFPS increases beyond approximately 60%, oxygen diffusion into the soil is restricted and anaerobic conditions are developed, promoting denitrification activity. Bateman and Baggs (2005) compared N_2O production during denitrification, autotrophic nitrification and heterotrophic nitrification in a fertilized silt loam soil with a range of WFPS from 20 to 70%. At 70% WFPS, all of the N_2O emitted was produced during denitrification, but nitrification was the main process producing N_2O at 35-60% WFPS. Linn and Doran (1984) also identified increased anaerobic microbial activity above 60% WFPS. Bateman and Baggs (2005) stated that aerobic denitrification was the predominant N_2O producing process at water filled pore spaces as low as 20%. During aerobic denitrification, the first reduction step is not inhibited by oxygen unlike the membrane bound nitrate reductase of anaerobic denitrification (Bateman and Baggs, 2005). It was also noted that anaerobic denitrification may have been occurring in anaerobic microsites at this low WFPS (Bateman and Baggs, 2005).

The type of applied nitrogen (NO_3, NH_4 or organic N) influences nitrification and denitrification since organic nitrogen, which is abundant in manure fertilizers, often also contains easily available carbon which may serve as substrate for denitrifying bacteria (Van Groenigen, 2004). Similarly, the type of land use can influence the transformations

during nitrification and denitrification because intensively cultivated low organic matter soils typically have less readily available carbon substrates for denitrifying bacteria than soils of higher organic matter content (Van Groenigen, 2004).

2.2.2 Carbon Transformations

Carbon compounds are abundant in both the soil and applied manure and are a source of energy for the microbial population. Autotrophic microbes (the majority of the nitrifiers) can use carbon dioxide (CO_2) as a carbon (food) source while heterotrophic microbes (the majority of the denitrifiers) use organic molecules as a carbon source. After application, the carbon in manure may be mineralized into CO_2 or converted to methane (CH_4) (NRCS, 2007). Bacteria and fungi in the soil mineralize carbon into CO_2 under aerobic conditions and methanogens produce CH_4 in very oxygen limited conditions. Under aerobic conditions, most soil microbes can use oxygen as an electron acceptor and break down the dissolved organic compounds and release CO_2 to the atmosphere (Li, 2007). Some of the CO_2 may be retained in soil gases and some of the carbon is bound into the soil as humic acid (NRCS, 2007). Since microbes that break down carbon also require nitrogen for production and growth, available nitrogen can become immobilized and is not usable by plants if there is an abundance of available carbon present.

Powlson et al. (1997) noted that net methane fluxes are determined by the balance between production (by methanogenic bacteria) and consumption (by methanotrophic bacteria). Methanogenic bacteria are very strict anaerobes (Knowles, 1993) while methanotrophic bacteria are aerobic and have the ability to use methane as their sole carbon and energy source (Brigmon, 2001). Both the production and consumption of methane may occur in the same soils (i.e.: production in an anaerobic zone below the water table or in microsites, and consumption in aerobic layers or microsites) (Powlson et al., 1997). Much of the methane generated in soil is oxidized before it reaches the atmosphere. In the soil, methane is oxidized to CO_2 or assimilated into the microbial biomass, but the sink strength and carbon transformations are affected by land management, nitrogen fertilizers and soil pH (Powlson et al. 1997).

Nutrient transformations result in forms of nitrogen and carbon that are susceptible to various forms of transport including runoff, leaching or volatilization. Nutrient losses mean fewer nutrients for the plants and an increased risk of environmental contamination. The risk of nutrient losses can be limited by applying the correct amount of nutrients required by the crop and applying them when and where the plants can effectively utilize them.

2.3 Environmental Impacts of Manure Application

When properly managed, land application is an environmentally responsible way to recycle manure nutrients. However, focusing only on nutrient recycling from manure application can result in the effects of other effluent constituents, such as microbial pathogens, heavy metals, and odorants being overlooked (Wang et al., 2004). Therefore, care must be taken to avoid nutrient overload which may have negative environmental impacts on the soil, water and air surrounding application sites. To avoid environmental risks, the most important factors to consider are the timing and rate of the organic fertilizer application. Matching application rates with the requirements of the soil and crop and applying the nutrients when the crop will use utilize them most efficiently dramatically reduces the risk of nutrient build-up, runoff and excessive gas emissions. Other considerations that impact the environmental risk of manure application include the type of manure, method of application, soil and weather conditions, and the type of cropping system. The following sections discuss these considerations in the context of their impacts on the soil, water and air quality surrounding application sites.

2.3.1 Impacts on Soil

The nutrient value of manure means this resource can be used to offset the cost of synthetic fertilizers. But manure and other organic amendments provide other benefits to the soil such as improved soil tilth and quality that are not always immediately apparent.

However, there are some detrimental effects such as nutrient build up that must be managed through proper timing and application rates (Schoenau and Assefa, 2004).

Adding manure and other organic fertilizers to soil promotes the development of more stable aggregates by increasing the organic matter content. More stable aggregates reduce losses to wind and water erosion and improves soil aeration and water holding capacity. Organic fertilizers have also been shown to reduce bulk density of soil and hardpan over time (Schoenau and Assefa, 2004). These benefits lead not only to increased yield, but also improved soil quality, an important and long-term goal of agricultural producers.

While comparing the effects of organic fertilizer application with mineral fertilizer application, researchers have discovered that organic manure application resulted in higher soil organic carbon and increased the soil's ability to sequester carbon (Ding et al., 2007). Almost all studies comparing manure application with no fertilizer application saw increased levels of organic carbon and total nitrogen in the top soil layer (Kingery et al., 1994). In addition to increasing nutrient levels in the soil, carbon and nitrogen mineralization and transformation rates were generally higher in soils applied with organic fertilizer than in soils applied with mineral fertilizers (Flavel and Murphy, 2006; Ding et al., 2007), generally resulting in an improved environment for plant growth if these transformations occur when the plants require them. Applying manure also tends to shift soil pH towards neutrality, whether in acidic or alkaline soils, thus improving nutrient availability (Schoenau and Davis, 2006). As manure applications improve the environment for plant growth, they may also improve conditions for beneficial microorganisms, such as those that mineralize N into plant available forms (Schoenau and Davis, 2006). In a long term study of the effects of organic and inorganic (mineral) nitrogen fertilizers, Meng et al (2005) noted that manured soils had higher organic C and N contents but lower pH and bulk densities than soils that had received various mineral fertilizers.

Application of commercial inorganic fertilizers like anhydrous ammonia, urea and ammonium nitrate allow more precise application of nutrients, but organic fertilizers

offer the benefit of "slow release" nutrients. The nutrients in organic materials like animal manures and compost are present in both organic and inorganic forms. Inorganic forms are usually immediately available to plants while the organic forms break down over time and become available to the plants after application. The release may not be complete until several years after application. While the ammonium N in manure may be considered entirely available for plant utilization, only a portion of the organic N (20-30%) will mineralize over the growing season (Qian and Schoenau 2000a in: Schoenau and Davis, 2006). This "slow-release" of nutrients results in reduced rates of supplemental fertilizers for several years after the use of organic materials. Along with providing a direct source of carbon for soil organisms, organic amendments provide an indirect carbon source via increased plant growth and plant residue returns (Bunemann et al., 2006). In the end, organic fertilizers help soil provide a better environment for plant growth and these effects are longer lasting than with the use of commercial fertilizers.

Of course, there are some cautions when applying manure. The nutrient content of organic fertilizers is highly variable, of relatively low concentration and often not in the relative proportions required by plants. Adding to this problem is the fact that organic fertilizers are heterogeneous, making it almost impossible to evenly apply the nutrients across the field. In addition, some organic materials are treated as a waste product and applying the material to the field is a means of disposing of the material, resulting in application rates that greatly exceed the nutrient requirements of the plants. If the nutrients applied to the soil are not used by the crop they will accumulate in the soil. Numerous studies have reported on the effects of elevated phosphorus, potassium, calcium, and magnesium contents in the top layer of the soil after repeated and long-term application of manures (Wang et al., 2004; Kingery et al., 1994). With some organic materials, such as biosolids or coal combustion by-products, heavy metal buildup in the soil can also cause concern (Shumann and Summer, 2004). Buildup of nutrients and heavy metals in the soil can result in plant toxicity or leaching and contamination of water sources in the vicinity of the application site.

The easiest way to avoid nutrient accumulation in the soil is to match the application of the nutrients to the requirements of the soil and crop. By testing the nutrient composition of the manure and soil and predicting the nutrient requirement of the crop, over-application may be avoided. However, the nutrient balance in organic materials is not in the same proportion required by most crops so over or under-application of at least one nutrient is unavoidable. In the past, manure application rates have been chosen to meet the nitrogen requirements of the crop. But this often results in the over-application of phosphorus, resulting in phosphorous accumulation in the soil (Hooda et al., 2001 and Wang et al., 2004) which can result in eutrophication of surface waters. Application rates that meet the phosphorous requirement of the crop can often result in under-application of nitrogen, requiring supplemental application of a concentrated nitrogen source. Osei et al. (2000) concluded that moving from nitrogen to phosphorus-based manure application rates could significantly reduce phosphorus build-up at moderate cost to producers. Even greater phosphorus load reductions could be realized by composting the organic material before application, but the composting process results in higher costs to producers (Osei, et al., 2000). Phosphorus-based application rates often require supplemental N application and larger areas are required to dispose of all available manure. Sometimes the amount of land required for P-based application rates is not available or economically feasible.

The method of application can also influence the impact of organic fertilizer application on soil quality. Subsurface application (injection or incorporation) disturbs the soil which can be either beneficial or detrimental, depending on the existing soil conditions. As already discussed, the concentration of nutrients in organic fertilizers is relatively low so a large volume of the material is required to meet nutrient requirements. Therefore, subsurface application of manure requires significant disturbance of the soil to accommodate the large volume of material. Heavy equipment traffic on sensitive soils may also lead to excessive soil compaction (McBride et al., 2000 in: Lague et al., 2005). Reduced tillage operations are favoured for soils at high risk of wind or water erosion so subsurface application of heterogeneous organic fertilizers may not be recommended in some cases (Laguë et al., 2005). On the other hand, injection or incorporation of organic

fertilizers can be useful for soil reclamation purposes by reducing hardpan and the bulk density of the topsoil. Furthermore, subsurface application results in better nutrient placement and Chen et al. (2001) reported an increase in yield due to injection of liquid manure because the nutrients present in the manure were more readily available to the plants. Mooleki et al. (2002a) (in: Schoenau and Davis, 2006) also concluded that, regardless of opener type, injecting the manure in bands gave higher crop yield and N recovery compared with broadcasted and incorporated treatments due to improved placement of nutrients. Finally, the level of soil disturbance can affect the size and orientation of the macropores in the topsoil, influencing the ability of water to flow through the soil.

2.3.2 Impacts on Water

Nutrient build-up in the soil can be toxic or harmful to plants, but an even larger danger is the potential for leaching or runoff and subsequent surface and ground water contamination. Nitrate leaching, phosphorus accumulation, eutrophication of surface waters, and pathogen and bacterial contamination of groundwater have all been reported as a result of poor manure management and land application practices. Water contamination poses serious human and animal health risks. Again, matching application rates and timing to the requirements of the soil and crop is critical to reduce the risk of environmental hazards. Other important considerations that impact the risk of water contamination after organic fertilizer application are the time between application and a rainfall event, soil conditions, topography, and the mode of application.

The timing of application plays a large role in protecting water quality when using manure as a fertilizer. If the nutrients are applied in the spring or summer when they will be quickly used by the crop, there is little chance for leaching or runoff. Fall applications may be convenient to have an empty manure storage for winter, but the nutrients will not be utilized until spring, increasing the amount of time for nutrient transformations and losses. Winter applications to frozen soil are problematic because the nutrients stay on the

soil surface until spring thaw where spring runoff is likely to carry away a large portion of the nutrients and deposit them in nearby bodies of water (Muller et al., 1997 in: Webb et al., 2001; Wagner-Riddle et al., 1998). Spring applications are most desirable since the nutrients can be quickly used by the germinating crop. However, the higher soil temperatures in spring result in high levels of microbial activity, increasing the rate of nutrient transformations that promote nutrient losses.

Application to soil immediately after or before a large rainfall event is also a risk for water contamination. Application after a rainfall when the topsoil may be saturated can increase the risk of runoff as infiltration of nutrients will be slowed. Rainfall can wash away nutrients on the surface or force them below the root zone and pose a major risk of bacterial and contamination of groundwater (Joy et al., 1998). Smith et al. (2007) suggested that organic fertilizers might be more environmentally sustainable than inorganic fertilizers, provided runoff events do not occur soon after application.

The amount of contaminants available for leaching or runoff is obviously related to the application rate. In some areas, it is quite common to double or triple the recommended application rate based on N requirements and apply every 2 or 3 years instead of annually. However, in an experiment that doubled the recommended application rate of hen manure, Flavel and Murphy (2006) measured elevated levels of nitrate and phosphate concentrations in subsurface drain water in comparison to recommended application rates of hen manure and commercial fertilizer. Joy et al. (1998) suggested that excessive application rates can result in significant ground and surface water contamination by bacterial and other contaminants in the manure. Chinkuyu et al. (2002) reported that application rate of solid manure had no significant effect on surface runoff water from corn plots but Hao et al. (2004) stated that applying excessive amounts of any livestock manure to agricultural land may increase the risk of phosphorous loading to surface water. Flavel and Murphy (2006) concluded that application rates should be reduced to minimize leaching losses in regions where ground water quality is of a concern.

The mode of application is another key factor to control water contamination risks. Gupta et al. (1997) reported that the total nitrogen, total phosphorus, ammonium nitrogen and nitrate nitrogen concentrations were lower in runoff generated from disk-tilled plots compared to that from the no-till plots applied with liquid swine manure. However, Rotz et al., (2007) reported that, in a simulation study, nitrate leaching losses were increased after immediate incorporation of dairy manure. In another study, surface broadcast manure application resulted in significantly higher bacteria concentrations in runoff water compared to the injected and commercial fertilizer treatments (Wang et al., 2000). Generally, surface applied materials are at greater risk for runoff events (such as an immediate rainfall) so subsurface application may be recommended to protect surface water sources. However, injection of high application rates to soils with high water conductivities or a high water table may put groundwater sources at risk.

Subsurface application can also affect the hydraulic conductivity of the soil by disturbing the macropores present in the top layer of the soil (Geohring et al., 2001). The size and continuity of the macropores dictate the type of water movement in the soil. Geohring et al. (2001) reported that plowing-in manure promotes matrix flow, resulting in reduced nutrient transport and lower concentrations in the drainage effluent. Une and Goss (2006) reported that the type of manure applied (solid vs. liquid) can also affect the type of flow within the soil. The authors stated that solid manure applications favoured matrix flow over macropore flow thereby increasing the water storage in the soil which tended to reduce the likelihood of runoff (Une and Goss, 2006).

The soil conditions and type of cropping system at the time of application also play a role in the risk of water contamination. Cover crops or saturated soils may inhibit the immediate infiltration of nutrients from organic fertilizers, making the area susceptible to rainfall runoff. In areas with high annual rainfall, management practices such as contouring, strip cropping, conservation tillage, terraces and buffer strips may be used to control runoff. In some cases, secondary containment systems, sedimentation basins, or ponds may be necessary to collect runoff (Gilley et al., 2002). Through proper

management, manure can serve as a valuable nutrient source and soil amendment without causing environmental concerns (Gilley et al., 2002).

2.3.3 Impacts on Air

The impact of organic fertilizer application on air quality does not have the same human-health implications as water quality issues, but odour and ammonia emissions from manure spreading are still considered a nuisance to the neighbours and can have an impact on the sustainability of the industry. In fact, Jenkinson (2001) suggested that, in the long term, gaseous emissions may eventually prove to be more environmentally damaging than impacts on the soil and water. Nitrous oxide (N_2O, a potent greenhouse gas) is produced naturally in soils through nitrification and denitrification, but agricultural practices such as fertilizer and manure application, cultivation, legume cropping and irrigation can increase N_2O production and emissions above background levels (Del Grosso et al., 2006). In fact, fertilizer application to agricultural soils is one of the main sources of nitrous oxide emissions in Canada (Banham and Haugen-Kozyra, 2004), making greenhouse gas emissions from manure application a concern. Applying the material under the soil surface can minimize some offensive emissions but requires more energy, may not be feasible for all organic amendments, and may promote the generation of different types of gases. Gaseous emissions of N from manure applications generally occur through volatilization of ammonia and loss of N_2 and N_2O through nitrification-denitrification processes (Sharpe and Harper, 2002). These emissions are affected by waste characteristics, method of application, climatic conditions, and chemical and physical soil properties. Other variables that impact the gaseous emissions from land application of organic fertilizers are the application rate and type of manure applied.

Land application of manure produces odour and ammonia emissions of very high concentration for relatively short durations. In most cases, odours from spreading organic fertilizers return to background levels within a day or two. However, GHG emissions from soil applied with organic fertilizers can be elevated for several years after

application, depending on the soil conditions and rainfall events. Ginting et al. (2003) noted that elevated emissions of GHG not only affects climate change but also to an increased risk of soil carbon and nitrogen depletion. In the long run, this could lead to the deterioration of soil health previously derived from the manure application (Ginting et al., 2003). While Sherlock et al. (2002) noted elevated nitrous oxide emissions for up to 90 days following application of pig slurry compared to an unfertilized plot, Ginting et al. (2003) found no residual effects of solid manure and compost application on GHG emissions up to 4 years after application compared to synthetic fertilizer and control plots. Therefore, the elevated GHG emissions from organic fertilizers may be no worse than the emissions from land applied with commercial fertilizers.

Applying manure under the soil surface either by incorporation or injection is the most effective way to reduce ammonia and odour emissions. Less contact area between the manure and air results in lower volatilization rates. Nitrogen volatilization is also influenced by the ammoniacal-N concentration, rainfall, temperature, manure pH, water content and application rate (Schoenau and Assefa, 2004). Surface applied manures can lose up to 75% of the ammoniacal-N to volatilization within seven days (Beauchamp et al., 1982 in: Schoenau and Assefa, 2004) and numerous studies have reported on significant odour and ammonia emission reductions due to subsurface application of liquid manures and co-fermented slurries (Hanna et al., 2000; Pain et al., 1991; Lau et al., 2003). However, Pain et al. (1991) concluded that no reduction in total emissions was detected when incorporation was delayed for 3 to 6 hrs after slurry application so injection or immediate incorporation is required to reduce gaseous losses after application. The depth of injection may also influence the amount of emissions from injected fields (Rahman et al., 2004). The authors found that odour emission rate increased significantly with increased injection depth and attributed this to the reduced amount of soil covering that resulted from the deeper injections. High volatilization losses lead to lower N availability (Beauchamp, 1983, Safley et al., 1980 in: Schoenau and Assefa, 2004) and contribute to odour emissions and acid deposition (Wulf et al., 2002b).

Several studies have noted increased GHG emission rates from organic fertilizers applied below the soil surface compared to surface applied materials (Wulf et al., 2002a, 2002b; Agnew et al., 2008). The anaerobic conditions below the soil surface may promote the denitrification process, whose byproduct is nitrous oxide. Surface applying the material avoids the generation of excessive nitrous oxide emissions but allows ammonia volatilization and odour emissions. In terms of carbon dioxide equivalents, the increase in nitrous oxide emissions after injection might be as high as the reduction of ammonia losses or, as in the case of injection on grassland, might even increase overall GHG emissions (Wulf et al., 2002a). Nevertheless, it should be considered that detrimental effects of ammonia also include acidification, eutrophication and odour (Wulf et al., 2002a).

The application rate of the organic amendment also plays a role in the quantity of emissions from fertilized land. In the case of ammonia volatilization, manure application rate does not have an effect on the proportion of ammonia loss, but the total amount lost increased with increasing rates of application (Hoff et al., 1981 in: Schoenau and Assefa, 2004). Rahman et al. (2004) found that odour emissions from manure injection did not change with application rate. Some data (Agnew et al., 2008) suggest that total GHG emissions from agronomic application rates of liquid and solid manure were not significantly different from emissions from unfertilized soil. Doubling and tripling the recommended application rate significantly increased overall GHG emissions. The same data suggest that the different types of organic fertilizers (liquid vs. solid) have different potentials for overall emissions. In general, liquid manure applications resulted in higher odour and GHG emissions than solid manure applications (Agnew et al., 2008).

Some research has shown that repeated applications of mineral fertilizers can affect the ability of the microbial population to oxidize (uptake) methane, another potent greenhouse gas (Steudler et al., 1989; Schimel and Gulledge, 1998 in: Jarecki et al., 2008). Hansen et al. (1993) also found that the addition of fertiliser nitrogen led to a decrease in CH_4 uptake by the soil. This was attributed to competition between NH_3 and CH_4 for the same active site of monooxygenase enzymes which catalyse the first

oxidation step of CH_4 and NH_4^+ in methanotrophs and nitrifiers (Hansen et al., 1993). In addition, the ability of a microbial population to oxidize methane is influenced by the soil pH. Acidic soils, which can be a result of mineral fertilization, generally show little or no methane oxidation (Powlson et al., 1997). However, the effect of acidity varies, suggesting that it is not the acidity itself that affects methanotrophs but other changes that sometimes accompanies acidification (Boeckx, 1997).

Powlson et al. (1997) also showed that long-term application of ammonium based commercial fertilizer (144 kg N/ha per year for 150 years) reduced methane uptake by 50% compared with soil receiving no fertilizer. However, during the same period, applications of solid manure (35 t/ha per year for 150 years) had no inhibitory effect on the soil's ability to oxidize methane despite the fact that the manure contained more N (240 kg N/ha per year) than the commercial fertilizer. Therefore, the form of the N applied has a significant effect on CH_4 metabolism. One explanation for this could be the larger microbial biomass on manured plots that rapidly removes the ammonium, reducing the acidifying effect of fertilizer application. Another explanation could be that ammonium is released more slowly from manure compared with the instantaneous addition of ammonium from inorganic fertilizer (Powlson et al., 1997).

The timing of manure applications can also influence the emissions surrounding an application site. Spring or early summer applications usually result in efficient nutrient utilization by the crop, but microbial activity is highest in warm soils and application of N to warm soils is usually considered to increase gaseous emissions. Additionally, since soil water content also influences the nutrient transformations, wet conditions in spring can promote denitrification. Rochette et al. (2004) reported higher N_2O emissions following spring applications of manure and commercial fertilizer than fall applications. The authors attributed the difference to the increased nitrification and accumulation of nitrate nitrogen (NO_3-N) after the spring application to warm soil. Subsequent rainfall increased the soil water content, promoting denitrification of the NO_3-N. The fall applications did not experience significant nitrification and accumulation of NO_3-N, limiting the production of N_2O. However, N lost to ammonia volatilization or runoff was

not measured from the fall applications or accounted for in the comparison so total losses between spring and fall applications may be similar. Fluxes of CO_2 and cumulated carbon dioxide carbon (CO_2-C) losses were also greater for spring than for fall applications (Rochette et al. 2004). Watanabe et al. (1997) also noted lower peak N_2O and CO_2 fluxes after winter applications of swine and cattle manure than autumn applications, likely due to the lower soil temperature during the winter applications.

2.4 Summary

Manure application can provide the soil with nutrients required to sustain healthy crop growth, but poor application practices have the potential to negatively impact the soil, surface, and groundwater and air quality surrounding application sites. The nutrients in manure and soil are transformed via microbial activity into certain forms of nutrients which can be environmentally hazardous. Nitrate nitrogen can pollute surface and groundwater, posing a human health risk, ammonia emissions lower the N availability to crops, while nitrous oxide and methane contribute to the greenhouse gas effect. Balancing the N loss dynamics from fertilized soil is very difficult. In general, practices that reduce the amount of N lost to volatilization result in more N in the soil, increasing the area of land required to apply manure at agronomic rates. If producers fail to account for the increased percentage of N applied when incorporating or injecting, they increase the susceptibility of the N loss via leaching. However, the nutrient transformations are affected by the soil environment such as air and water content, pH, and labile carbon content. All of these soil environmental factors can be influenced by manure application practices such as application rate, timing and manure placement. Knowledge of how these management practices affect the soil environment can help producers make management decisions that reduce the likelihood of soil, water and air contamination from manure application.

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Chapter 3

3.0 Odour Emissions from Manure Spreading

Land application of manure is a common method of manure handling in which the nutrients are returned to the soil. However, odours from manure application activities can hinder the expansion of the livestock industry because of the potential nuisance to neighbours. The objective of this study was to assess the effectiveness of subsurface application at reducing odours from manure spreading for both solid and liquid manure. Flux chambers and dynamic dilution olfactometry were used to assess odours from five livestock manure species applied at three application rates using surface and subsurface application methods. The results of the study indicated that odour concentrations from injected plots were up to 66% (37% on average) lower than concentrations from broadcasted applications. Injection seemed to have a larger impact on reducing odours from solid manure than liquid manure, mainly due to better manure coverage from solid manure injection. Odours from solid manure applications were also 37% lower than from liquid manure applications. In general, odours from liquid and solid manure increased with higher application rates, but there was little difference among one, two and three year application rates. The specific odour rate decreased with higher application rates due to the reduced surface area available for volatilization of compounds with higher application rates. Higher application rates did result in higher overall odour concentrations, but this increase was not proportional to the amount of N applied. Based on the results from this study, injection of manure is an effective way to reduce the overall odour emissions from manure spreading, particularly for solid manure. However, other factors associated with manure injection, such as the increased power requirement

and soil disturbance, as well nutrient transport and greenhouse gas emissions, must be considered when evaluating the overall impact of manure injection versus surface application.

3.1 Introduction

Land application of animal manure is an efficient and effective way of recycling important by-products from livestock production. Manure nutrients benefit soil crop-systems by building up and maintaining soil fertility. In addition, manure can also improve soil tilth, increase its water-holding capacity, lessen wind and water erosion, and improve aeration, and promote the establishment and growth of beneficial organisms (Schoenau and Assefa, 2004).

Virtually all of the 150 million tonnes of manure produced annually in Canada are land applied with almost 3.5 million hectares being treated with manure in 2005 (Statistics Canada, 2006). Manure spreading typically occurs during the spring and/or fall seasons to accommodate the manure production and storage as well as the field crop cycles. In some cases where the manure storage is of insufficient size, manure spreading may occur throughout the year. While manure spreading produces odours of short duration, these are considered more intense and more unpleasant than odours from the barns or manure storages. In fact, more than half of all complaints about intensive livestock facilities result directly from odour emissions following land application of manure (Choinière et al., 2007). Exposure to livestock odours is also a potential health concern (Schiffman and Williams, 2005). Odours are the main concern in communities where the development of a new livestock facility is proposed (Bickert, 2003).

In order to allow for the sustainable growth of the livestock industry, odour emissions associated with livestock production must be reduced. A range of gaseous emission mitigation strategies have been developed across the different manure management stages, and land spreading is the source where the most cost-effective strategies can be

employed (Huijsmans et al., 2004). These mitigation strategies consist of alternative slurry application techniques and rapid incorporation of manures into the soil after application (Misselbrook, 2003). Since volatilization is the dominant transport mechanism contributing to odour emissions after manure spreading, reducing the contact area between the manure and the atmosphere will theoretically reduce odour emissions. However, objectively determined values of the odour reduction potential of these practices, particularly for solid manure, are limited since very little research has been dedicated to odour measurement after application of solid manure. Additionally, the set-back distances between land applied sites and neighbours in Saskatchewan are not based on scientific data since odour dispersion and intensity data after land application are not available for the Saskatchewan climate. Improved set-back distances based on scientific data will increase the area of land available for land application while reducing the odour nuisance to neighbours, allowing for environmentally sustainable growth of the industry.

Establishing science-based set-back distances typically involves dispersion modeling. Well established point source dispersion models can be modified to handle area sources such as manure spreading. In order to predict odour surrounding application sites using dispersion models, detailed meteorological information is required along with reliable odour emission rates from the source. Source emission rates from manure spreading will vary over the first few hours after application and the magnitude and variation will depend on the type of manure, application rate, and application method. This information is currently unavailable and is required in order to apply dispersion modeling to manure spreading activities.

If information regarding the odour emissions from different application techniques and the emission rate trend over the first few hours after application becomes available, then set-back distances for manure spreading can be established to minimize the odour nuisance to neighbours while maximizing land-use efficiency. Properly sited and operated, livestock facilities create on-farm job opportunities, are an important contributor to the economic wealth of the province and nation, and pose no health or environmental risks for the community.

3.2 Literature Review

3.2.1 Method of Odour Measurement

Livestock odours are made up of over 200 volatile organic compounds (phenols, indoles, skatoles, etc., Qu and Feddes, 2004). The combinations or interactions of two or more of these compounds often contribute to the odour of a sample even more than the concentration of the individual gases themselves. Since odour is so complex, there are several odour indices available for odour quantification: odour strength (concentration and intensity), hedonic tone, character, and persistence (St. Croix Sensory, 2007). Currently, the accepted tool for odour quantification is the human nose. Since human odour perception is very subjective, with individuals having different odour sensitivities, thresholds and tolerances, odour measurement can be highly variable.

3.2.1.1 Odour Strength by Olfactometry

Odour strength (concentration) is directly related to the number of dilutions of fresh air required to bring the odorous air sample to its detection threshold (based on 50% panelist recognition). The higher the threshold value, the more dilutions are required to bring the odor to threshold, and thus the stronger the odour (St. Croix Sensory, 2007). Thus, the odour threshold can be defined in terms of a dimensionless dilution ratio. However, the pseudo-dimension of "Odour Units" (OU) is often used. Units of "Odour Units per cubic meter" (OU/m^3) are also commonly applied in order to calculate odour emission rates (St. Croix Sensory, 2007).

Olfactometers are standardized instruments for the measurement of odour concentration (Feddes et al., 2001) using the dilution to threshold method. The 8 port olfactometer at the University of Alberta, designed according to ASTM and CEN 13725 (2003) standards, is a dynamic triangular forced-choice olfactometer and can provide odour concentration and hedonic tone (offensiveness) measurements. With these olfactometers, panellists are presented with three air samples: two of the samples are odour-free air and

once contains diluted odour (Feddes et al., 2001). The panellist must choose one of these as a "forced choice" and indicate whether the choice is a guess, a detection or a recognition. The dilution threshold (concentration) is established when 50% of the panellists have correctly identified the odour sample from the odour free samples (Choiniere and Barrington, 1998 in: Feddes et al., 2001). The panellists also rate the hedonic tone of the sample after the threshold has been reached.

3.2.1.2 Odour Intensity by Nasal Rangers(TM)

Olfactometers can provide a standardized measurement of odour concentration, but olfactometry analyses require that samples be collected and transported to an olfactometry lab. These samples are often not representative of the odours actually experienced in the field due to instantaneous shifts in wind direction and speed and bursts of odour emitted from the source. The method of measuring odour directly in the field developed by St. Croix Sensory Inc. (Lake Elmo, MN, USA) uses trained human odour assessors (Nasal Rangers™) to quantify odour intensity, or the relative strength of the odour above the recognition threshold (St. Croix Sensory, 2007). The "relative" strength is defined by the standardized 8 point n-butanol reference scale (ASTM, 1997). Other studies have focused on the measurement of odour intensity using a modified, 5-point scale (Guo et al., 2001a). The differences between these scales are presented in Table 3.1.

Table 3.1. 8-point and 5-point n-butanol reference scales for odour intensity measurement.

8-point Scale (ASTM 1997)			5-point Scale (Guo et al. 2001a)		
Intensity Level	**Annoyance**	**n-butanol in water (ppm)**	**Intensity Level**	**Description**	**n-butanol in water (ppm)**
0	no odour	0	0	no odour	0
1	not annoying	120			
2	a little annoying	240	1	very faint odour	250
3	a little annoying	480			
4	annoying	960	2	faint odour	750
5	annoying	1,940	3	moderate odour	2,250
6	very annoying	3,880			
7	very annoying	7,750	4	strong odour	6,750
8	extremely annoying	15,500	5	very strong odour	20,250

While extensive training and use of the reference scale remove some of the subjectivity related to odour assessment, results from human sniffers in the field tend to be highly

variable. Also, coordinating assessors in the field during allowable weather conditions (based on temperature and wind speed and direction) can also be challenging. Finally, odour intensity is a "dimensionless" value that cannot be easily compared with other odour intensity studies because protocols and assessors are not always identical.

St. Croix Sensory Inc. has also developed a field olfactometer, or Scentometer$^{(TM)}$, for the measurement of odour strength (dilution to threshold ratio) directly in the field. The olfactometer creates a calibrated series of discrete dilutions by mixing the odorous ambient air with odour-free (carbon) filtered air. Field olfactometry defines each discrete dilution level as a "Dilution to Threshold" (D/T) ratio where D/T is defined as the volume of odour-free air divided by the volume of odourous air (Hamel et al., 2004). This method allows the collection of odour concentration directly in the field, eliminating the need for chamber collection. However, issues with the sampling timing and missed wafts of odour make the field olfactometer results inconsistent. Attempts have been made to standardize measurement techniques in the field during and after land application of manure by Hamel et al. (2004), Brandt et al. (2008), and Sheffield (2005).

3.2.1.3 GC-MS and Electronic Nose (E-nose)

Two of the main issues relating to odour measurement are the subjectivity of the human nose and the effect of odour component mixtures. It would be advantageous to combine two or more different measurement techniques, such as gas chromatography (GC) and olfactometry to simultaneously assess the chemical composition of a sample along with the character and odour concentration. The combination of measuring odour and odorants is called gas chromatography-olfactometry-mass spectrometry more commonly called GC-MS Sniffer (UNSW, 2009). Assessment of odour samples by GC-MS Sniffer technology is a specialized and costly procedure.

Electronic noses (E-noses) usually consist of an array of electronic chemical sensors selected to detect specific components and combinations in an odour sample. These electronic devices produce an almost instant response which is useful in many applications such as the food or perfume industries. However, because of the large

amount and variety of volatile organic compounds that make up manure odour, in addition to the synergistic mixing effect of manure compounds, E-noses are not well suited for manure odour assessment. Some studies have confirmed the detection of farm odour and the response to odour concentration for some electronic noses (Nimmermark, 2001). Misselbrook et al. (1997) used an E-nose to measure odour concentration following application of cattle slurry to grassland and they demonstrated that the E-nose responded linearly to odour concentrations arising from cattle slurry applications. Alternatively, several researchers have noted that E-noses are only effective at assessing manure odours of very high concentration (Hobbs et al., 1995; Persaud et al., 1996) or they may not be sensitive to the particular compounds causing odour (Gralapp et al., 2001). More recently, Qu et al. (2008) showed that integrating results from an AromaScan A32S electronic nose and hydrogen sulphide and ammonia detectors produced odour concentration results that correlated with an olfactometer for samples collected from swine manure sources.

3.2.1.4 Other Odour Indices

Odour measurement is generally focused on odour concentration. In recent years, odour researchers have been careful to include measures of other odour indices such as hedonic tone, character and persistence. Hedonic tone is a measure of the pleasantness or unpleasantness of an odour and is sometimes measured by olfactometry. Once the panellist correctly identifies the presence of the odour at two successive dilution levels, hedonic tone is measured at the next (stronger) dilution level (D. Martineau, personal communication, 06/07). Therefore, each panellist may measure hedonic tone at a different dilution level, making direct comparisons between panellists difficult to interpret. Further complicating the measurement of hedonic tone, the standard method for measurement requires assessment of pleasantness of an undiluted sample. However, assessment of undiluted samples may cause nose fatigue in the panellists and require samples of large volume.

The character of an odour, also known as "odour quality," is reported using standard descriptor lists. Assessors report both what the odour "smells like" (e.g. sewer, banana,

etc.) and what the odour "feels like" (e.g. burning, tingling, cooling, etc.) (St. Croix Sensory, 2007). Persistency describes the rate at which an odour's perceived intensity decreases as the odour is diluted (McGinley et al., 2000). Specific odour compounds like sulphur appear to make an odour more persistent than components like nitrogen (Feddes and Clark, 2006). Other factors that influence an odour's annoyance are the duration and frequency of the odour event. For example, odours from manure spreading are unpleasant and intense but are often infrequent (2 or 3 times a year) while odours from livestock housing buildings and manure storages are less intense but almost constant throughout the year.

All of the odour measurement methods described above, except the E-nose, rely on the human nose. With proper training, such measurements can be accurate, reliable and, for the most part, objective. However, each odour index has a unique unit of measurement. Concentration is measured in OU or OU/m^3, intensity is an objective number on different reference scales, hedonic tone is a subjective number on yet another reference scale, character is usually a descriptive word or adjective, while persistence is a number that represents the exponent in Stevens Law (usually between -0.87 and -1.86 as reported by Ouellette et al., 2006). Choosing one odour index may not completely describe the odour but analyzing odour data that include different units of measurement and non-numeric results is very cumbersome.

3.2.2 Description of Methods for Odour Sampling

The method of odour collection will depend on the method of odour measurement and the goal of the odour research. For field measurements of odour intensity and odour dilution to threshold, assessors record odour data on site and samples are not required. Odour concentration, hedonic tone and persistence measured by olfactometry require samples to be collected in Tedlar bags (typically 10 L). Care must be taken to collect representative and consistent samples to ensure comparable results. Even when proper care is taken, results by olfactometry can be highly variable because human odour evaluation is

influenced by anxiety, distraction, fatigue, health status, personal comfort and/or visual cues (Brandt et al., 2008).

Gaseous emissions have been collected in a variety of ways. Non-point source odour emissions from manure-applied fields have been collected via static chambers (Hansen et al., 2006; Chen et al., 2001), dynamic chambers (Lau et al., 2003), wind tunnels (Lindvall et al., 1974; Rahman et al., 2004; Hanna et al., 2000; Pain et al., 1988, 1990; Misselbrook et al., 1997; Choinière et al., 2007; Moseley et al., 1998; Pahl et al., 2001), or by micrometeorological techniques (Phillips et al., 2000; Smith et al., 2007, Mkhabela et al., 2007; Pain et al., 1991).

3.2.2.1 Static Chambers (also called non-steady state or vented chambers)

The static chamber method involves allowing gas emissions to collect in a container of known volume for set periods of time. Samples are drawn at known intervals and the concentrations of the gases are measured and plotted versus time. The gas emission rate and concentration at time zero can then be calculated. Typically, static chambers are not used for odour emission measurement since the lack of sweep air allows concentration build-up in the chamber, potentially suppressing emissions. Additionally, for a single flux measurement, static chambers require collection and analysis of at least three subsamples. This is so the rate of increase of gas concentration over time can be analyzed to determine the gaseous flux. Odour concentration measurements are costly, so measurement of odour flux with static chambers is typically not feasible.

3.2.2.2 Dynamic Chambers

The dynamic chamber (also called a steady state, flow-through, or open chamber) is a sealed, open-bottomed chamber that is placed on the odour emitting surface. During operation, clean dry air is forced into the chamber at a fixed slow rate. Within the chamber, this air is mixed with the emitted odours by the physical layout of the device (in some chambers the mixing is aided by an impeller within the hood). The sample is drawn

from the chamber in the sample container, usually via a sampling lung or vacuum box, and the concentration of the emitted odour is measured in the sample bag by olfactometry (usually within 24 hours). Excess air is expelled to the atmosphere through a small vent in the chamber. This vent also maintains the pressure in the hood close to atmospheric pressure. Assuming complete mixing between the emissions and the sweep air, the emission rate can be calculated from the concentrations of the sample and the ambient air using a simple mass balance continuity equation (Equation 3.1).

$$f_o = \rho(C_{samp} - C_{amb}) * \frac{Q}{A} \qquad (3.1)$$

Where: f_o = gas flux (mg/m^2-s),

ρ= density of measured gas (kg/m^3),

C_{samp} and C_{amb} = concentration of sampled and sweep air, respectively (ppmm or OU/m^3),

Q = flow rate of sweep air (m^3/s), and

A = cross sectional area of chamber (m^2).

When using a dynamic chamber, particular care is required to ensure that the pressure inside the chamber is identical to the outside pressure (Smith and Watts, 1994a). One advantage of the dynamic chamber compared to the static chamber is the simulation of the microenvironment above the enclosed soil surface. When properly designed and operated, dynamic chambers maintain conditions within the chamber nearly the same as those in the surrounding field. Disadvantages of the dynamic chamber include the need to measure the gas concentration of the sweep air for the mass balance calculation, and potential for gas build-up in the enclosure, suppressing emissions from the surface. Alternatively, low emissions may be difficult to measure if the sample gas is diluted beyond the measuring capabilities of the gas analyzer. Additionally, the introduction of the sweep air can produce problematic air flow patterns, such as turbulent flow or stagnant zones within the chamber (Gao et al., 1997).

Several assumptions are required to determine emissions from dynamic chamber measurements. These include:

- airflow in chamber must be steady-state (i.e. the rate of air flow is not a function of time),
- gas flux must be uniform over the entire covered surface and during the sampling interval,
- the in-coming airstream and out-going airstream must be well mixed, and
- the diffusive flux is dominant and the advective mass flow is negligible (Gao et al., 1997).

Other factors affecting the rate of emissions as sampled by a dynamic chamber are:

- the small area of emitting surface enclosed by the hood does not account for spatial variation of emissions,
- the suppression of the turbulent transport mechanism that carries the emissions away from the emitting surface may result in gas concentration build-up, and
- imperfect mixing of the emissions and the sweep air provides erroneous results (Smith and Watts, 1994a).

The chamber method of emission measurement is very well suited for replicated treatment experiments with many factors since large or full scale applications are not required (Greatorex, 2000). However, care must be taken to ensure that full-scale conditions are simulated during the small scale experiments to ensure the information gained can be applied to real world scenarios. In addition, McGinn (2006) stated that chamber techniques are sensitive enough to quantify mitigation practices (i.e., the relative change in emissions), but they are not suitable to determine "true" emission factors or cumulative emissions as required for inventory work.

3.2.2.3 Wind Tunnels

Wind tunnels are a special form of dynamic flux chamber. Wind tunnels are portable, open-bottomed enclosures which are placed over the emitting surface. Ambient or filtered air is blown or drawn through the tunnel to mix with and transport the emissions away

from the emitting surface (Smith and Watts, 1994a). The selection of the appropriate wind speed to use in a wind tunnel is critical and should be reported whenever emission results from a wind tunnel are published. The main difference between wind tunnels and flux chambers is the specification of the airflow rate to simulate actual wind speeds and the laminar flow that usually exists within a wind tunnel. Generally, the air flow rate in a wind tunnel is much higher than the airflow rate in a flux hood, making the concentration measurement of low emissions with a wind tunnel difficult. The goal of the wind tunnel is to more closely simulate the natural air flow of the wind over the unenclosed surface and to prevent emission suppression due to concentration build-up under the cover (Hudson et al., 2009). Emissions of odours collected using wind tunnels are calculated using Equation 3.2.

$$E = \frac{OC * V * A_c}{A_s} \qquad (3.2)$$

Where E = odour emission rate, OU/m^2-s,

OC = odour concentration (OU/m^3),

V = velocity of air in the tunnel (m/s),

A_c = cross sectional area of the main chamber (m^2), and

A_s = surface area covered by the tunnel (m^2).

3.2.2.4 Comparison of Dynamic Chambers and Wind Tunnels

Some researchers have attempted to correlate odour emissions measured by a chamber with actual emissions (Navaratnasamy et al., 2005) and the difference in odour fluxes as measured by a dynamic chamber and a wind tunnel (Navaratnasamy et al., 2005; Hudson et al., 2009; Jiang and Kaye, 1996; Smith and Watts 1994a, 1994b). Navaratnasamy et al. (2005) compared odour emissions by operating a wind tunnel (flow rate 30 L/s) and a dynamic chamber (flow rate 1 L/s) with identical surface area dimensions (0.8 m x 0.4 m) on a reservoir of n-butanol (an alcohol used as an odour reference). This way, a theoretical "actual" emission rate could be calculated and compared with emission rates measured by the two chambers. Results from this study suggested that the odour concentration could be measured with relatively more confidence using the dynamic chamber method because the lower flow rate resulted in less dilution of the sample. The

emission rate from the dynamic chamber was also closer to the theoretically calculated emission rate (Navaratnasamy et al., 2005). For the wind tunnel, the theoretically calculated emission rates were lower than corresponding measured emission rates by a factor of 4 (Navaratnasamy et al., 2005).

Hudson et al. (2009) suggested that the performance of the dynamic chamber and wind tunnel depended on the physical differences of the surface from which measurements were collected (i.e.: wet vs. dry). The wind tunnel used in this study was 0.8 m x 0.4 m x 0.25 m and was operated at a wind speed of 0.3 m/s. The dynamic chamber was circular with volume of 0.03 m^3 and a surface area of 0.13 m^2 and was operated at an airflow rate of 0.0833 L/s. Odour samples were collected from a variety of surfaces (compost pile, uncovered anaerobic lagoon, covered anaerobic lagoon, dry feedlot pad, wet feedlot pad) and the emissions calculated from both chambers compared. Odour concentrations were consistently higher from the dynamic chamber while the calculated emission rates were higher from the wind tunnel (due to the higher airflow rate and lack of suppression of emissions). There appeared to be no relationship between emission rates calculated from each chamber when all the data were pooled, but when the data from different surfaces were separated, significant linear relationships between the two collected methods were formed for the feedlot pad sources and anaerobic lagoon sources.

Jiang and Kaye (1996) compared wind tunnel with dynamic chamber performance for the measurement of volatile organic compounds (VOC) emissions. A wind tunnel of undefined size was operated with a flow rate of 30 L/s to simulate surface wind speeds between 0.3 and 1 m/s while a dynamic chamber of undefined size was operated with sweep air flows of between 0.033 and 0.083 L/s. The emission rates measured using the two chambers were very similar for toluene (relatively high Henry's law constant (K_H) with units of Pa m^3/mol), but differed greatly for acetone and methyl ethyl ketone (relatively low K_H). This led the authors to conclude that dynamic chambers were suitable for measuring emissions of compounds with high K_H, regardless of whether this was expressed as Pa m^3/mol or in dimensionless form as a gas to aqueous (g/aq) ratio. When K_H is greater than 250 Pa m^3/mol (0.1009 dimensionless g/aq), volatilization is

liquid phase controlled. When K_H is less than 2.5 Pa m^3/mol (0.001009 dimensionless g/aq), volatilization is gas phase controlled. Jiang and Kaye (1996) concluded that dynamic chambers resulted in substantial underestimations of the emission rates, particularly when the VOC's exhibited gas phase controlled volatilization processes. For gas phase controlled processes, volatilization is strongly influenced by wind speed, so the sweep air in dynamic chambers is not a suitable representation of ambient conditions.

Smith and Watts (1994a, 1994b) examined odour emission rates from cattle feedlots and compared the literature values of odour emissions from manure spreading measured by dynamic chambers and wind tunnels. Smith and Watts (1994a) summarized the work in Pain et al. (1988) where wind tunnels were operated at 1 m/s and 3 m/s. Emission rates from the same source were higher when the velocity was 3 m/s due to the greater volume of air drawn through the tunnel at the higher speed. In their review of the literature, they noted that dynamic chambers resulted in consistently lower emissions than wind tunnels. The authors suggest that this is due to the buildup of gases in the chamber suppressing emissions due to the lack of turbulent transport away from the emitting surface (Smith and Watts 1994a). Smith and Watts (1994b) noted that air speeds must be specified whenever wind tunnel emission rates are cited and the wind tunnels should be operated at ambient wind speeds.

3.2.2.5 Micrometeorological Techniques

Traditional micrometeorological techniques involve real time measurement of gas concentrations at various heights downwind of application sites. Typically, a mass balance method equates the average surface flux density of gas from plots to the difference between the integrated horizontal flux at a known downwind distance and the upwind edge of the field (Sherlock et al., 2002). These techniques allow calculation of cumulative emissions (grams of gas per day) rather than fluxes (grams of gas per m^2 per hour).

At this time, real time measurements of odour concentration by olfactometry are not possible. However, simplified versions of the micrometeorological technique exist for

odour measurement. Smith et al. (2007), Mkhabela et al. (2007) and Pain et al. (1991) utilized the theoretical profile shape (TPS) method to estimate odour emissions based on an integrated product of the wind speed and gas concentration at a single height above the treated surface. For relatively small areas, the atmospheric stability is assumed to have a minimal effect on the ratio of the horizontal flux to the vertical flux from the ground (Smith et al., 2007). Therefore, samples can be collected from a single height (ZINST) as defined in Gordon et al. (1988). The ZINST value is dependent on the surface roughness length and is assumed to be homogeneous over the source area (Smith et al., 2007). The odour flux (OU/m^2-s) is then calculated using Equation 3.3.

$$Flux = \frac{OC * u}{k} \tag{3.3}$$

Where: OC = odour concentration of sample (OU/m^3),

u = wind speed (m/s), and

k = a constant as defined in Gordon et al. (1988) based on experimental parameters.

This method of odour emission measurement eliminates the need for chamber collection and is theoretically a more true representation of the odour in the air at the sample site. This allows the effect of meteorological variables such as temperature and wind speed on odour emissions to be determined (Mkhabela et al., 2007). However, odour samples drawn directly into bags from the air typically have low odour concentrations (<200 OU/m^3). Background odour concentrations of ambient air and Tedlar bags can be between 50 and 150 OU/m^3 (Moseley et al., 1998; Qu and Feddes, 2006), making it difficult to see statistically significant results from samples collected this way.

3.2.3 Manure Spreading Odour Emission Measurements in Literature

The methods for odour emission measurement from manure spreading are discussed here while the results from these studies are summarized in Table D.1 in Appendix D and discussed in Section 3.5 of this chapter.

3.2.3.1 Static Chambers

Odour concentrations from slurry-applied land using static chambers were reported by Chen et al. (2001) and Hansen et al. (2006). Single samples were collected from the chamber headspace so flux calculations were not possible. Hansen et al. (2006) used a chamber (3.12 m^2 and 1.87 m^3) and compared odour concentrations after applying untreated slurry, anaerobically digested slurry, and digested and separated slurry at a rate of 30 t/ha. Odour concentrations measured by Hansen et al. (2006) ranged from 150 to 1,000 OU/m^3 and, while no statistically significant results could be found due to high variability, the untreated slurry resulted in the highest odour concentrations, followed by the digested slurry and the digested and separated slurry (Hansen et al., 2006). The authors showed that odour concentration actually increased 4 hrs after application of slurry, presumably due to the increased soil and slurry temperature.

Similarly, Chen et al. (2001) used a semi-cylindrical "hood" that covered an area of 1 m^2 and compared odour concentrations after application of pig slurry using injection, slipper foot, aerated surface and dribble bar surface techniques. Odour concentration results obtained by Chen et al. (2001) ranged between 234 and 1094 OU/m^3 for the manure application treatments. Although the results were highly variable, the authors concluded that injection and slipper foot application resulted in lower odour concentrations than surface applications.

3.2.3.2 Dynamic Chambers

The earliest work on odour measurement by dynamic chambers (or wind tunnels) was by Lindvall et al. (1974). Instead of storing samples in bags, the authors used a mobile odour lab for odour concentration measurement in the field. A chamber of unspecified size and flow rate was used to collect samples after the application of untreated swine manure, aerated swine manure, swine manure treated with ammonium persulphate, swine urine, untreated cattle manure and composted cattle manure. Manure was "buried" via a harrow, plow and a disc harrow as well as injected using two types of machines. Current designs of wind tunnels used for odour research are based on this early "Lindvall Hood". Results from this study indicated that injection reduced odours compared to surface application and aerobic treatment and ammonium persulphate additives also reduced odours compared to untreated manure.

Lau et al. (2003) investigated odour emissions for manure spreading using a subsurface deposition applicator and liquid swine manure using a "surface isolation flux chamber" (0.0645 m^3 volume, 0.19 m^2 area) operated at 10 L/min. A splash-plate applicator and sub-surface deposition system were used for manure application (70,000 L/ha). The effect of time after application up to 2.5 hours was investigated. Odours from the sub-surface application were lower that from splash plate application.

3.2.3.3 Wind Tunnels

Wind tunnels have been used extensively for odour emission research. In the late-80's, Pain et al. (1988) used wind tunnels (1 m^2 at 1 m/s) to investigate the effect of manure type (pig slurry, cattle slurry, separated cattle slurry) on odour emissions over time after application. The odour concentration measured 24 h after application was considerably lower than the concentration measured 2 h after application (Pain et al., 1988). In Pain et al. (1990), the same wind tunnel was used to study the effect of anaerobically digesting pig slurry from two different diets on the odour emissions after application at 80,000 L/ha. While digestion reduced odours compared to raw manure, there was no difference in odour between the two diets (Pain et al., 1990). Misselbrook et al. (1997) compared odour emissions from spreading cattle slurry on grassland measured by a wind tunnel (1

m^2 at 1 m/s) with two E-noses. Measurements were taken up to 15 hrs after application. The authors noted that odour concentrations returned to background levels within 2 h of application (Misselbrook et al., 1997). Moseley et al. (1998) compared odour emissions after application of anaerobically digested sewage sludge and pig slurry. They applied manure using 3 different methods (surface, slipper foot and improved injector tine) and measured odour emissions 5 min and 24 hrs after application using a wind tunnel (1 m^2 at 1 m/s). They concluded that odours from slipper foot application were equivalent to surface application while odours from injection were lower and equivalent to background odours (Moseley et al., 1988).

Hanna et al. (2000) investigated the effects of application technique of liquid manure on odour emissions using the wind tunnel method (0.787 m^2 at 2.2 m/s). Samples were collected immediately after and one day after application. The highest odours came from broadcasted application while the "sweep application" resulted in odours similar to untreated soil. Odours returned to background levels within 24 h (Hanna et al., 2000). Pahl et al. (2001) used a wind tunnel (0.5 m^2 at 0.35 m/s) to compare emissions from surface applied manure and manure applied with a shallow injector. However, the study involved no replicates and no control and the results were highly variable, providing no statistically significant results. Rahman et al. (2004) used a wind tunnel (0.3 m^2 at 0.3 m/s) and reported on the effects of sweep injection tools on soil surface profile, manure exposure and odour emissions using 3 tools, 3 depths, 2 speeds and 2 moisture contents. The odour concentration actually increased with injection depth and the authors found no correlation between application rate and odour concentration (Rahman et al., 2004).

More recently, Choinière et al. (2007) developed a protocol using wind tunnels of unknown size and a wind speed of 0.3 m/s to examine the odour reducing potential after application of various manure and feed additives. The authors stated that the wind tunnel system provided statistically significant results, which is difficult to achieve in odour research due to the high variability of odour concentration measurements.

3.2.3.4 Micrometeorological Techniques

Although the micrometeorological theoretical profile shape (TPS) approach is commonly used for ammonia volatilization measurements (Gordon et al., 1988; Huijsmans et al., 2001), its use in odour emission measurements is still being studied (Pain et al., 1991; Mkhabela et al., 2007; Smith et al., 2007). Mkhabela et al. (2007) used this technique to study the effect of application rate, rainfall, meteorological conditions, and slurry dilution on odours after application of hog slurry. Doubling the rate had no effect on odours, but tripling the rate increased odours compared to a conventional rate (Mkhabela et al., 2007). Also, applying slurry to soil after a simulated rainfall increased emissions and slurry dilution decreased odour emissions slightly (Mkhabela et al., 2007). Smith et al. (2007) also used the TPS approach in their study of the effects of type of manure (solid vs. liquid), application rate, and rainfall on emissions over time after application of swine manure. The authors noted that liquid manure initially generated higher odour emissions but odour emissions from solid manure persisted for longer. Also, increased application rates and applying manure after a heavy rainfall generally produced higher emissions (Smith et al., 2007). Pain et al. (1991) examined the effects of slurry type (pig vs. cattle) and application method (surface, rigid tines, rotary harrow and plough) on emissions over time after application. The authors concluded that odour concentrations were greater for pig than for cattle slurry and worthwhile reductions in total emissions over 48 h was achieved only by immediate ploughing (Pain et al., 1991).

Phillips et al. (1990) used the micrometeorological method described in Denmead (1983) to analyze the effects of shallow injector, deep injector, trailing or hanging hoses (to place manure on soil surface but under residue cover), traveling irrigation gun and splash plate after application of slurry. Odour concentrations were measured up to 123 hrs after application so the emission rate trend over time could be observed. The highest odour concentrations resulted from irrigation gun application, followed by splash plate, deep injection, shallow injection, and trailing hoses (Phillips et al., 1990).

3.2.4 Dispersion Models

Establishing science-based setback distances for manure spreading should involve dispersion modeling. Air dispersion models are commonly used to predict the downwind movement of toxic gases from industrial sources. Since more than 60% of the air pollution complaints to regulators are related to odours (Leonardos, 1996), recent efforts have focused on assessing the suitability of using existing dispersion models to predict the transport and concentration of odours downwind of factories and intensive livestock facilities. The ability to predict the odour concentration surrounding such facilities will assist regulators in establishing separation distances to minimize the odour nuisance to neighbours and maximize the space available to expand the industry. Minimizing nuisance and using space more efficiently will help ensure the economic and environmental sustainability of the industries.

3.2.4.1 Models for Odour Dispersion

Guo et al., (2001b) and Zhou et al., (2005) summarized the air dispersion models applicable to odour dispersion modeling. The suitability for odour dispersion modeling of several models (ISC, AUSPLUME, CALPUFF) as well as several special models (AODM, INPUFF, fluctuating plume model) have been examined by researchers around the world (Piringer et al., 2004; Schauberger et al., 2000; Mussio et al., 2001; Xing et al., 2006). Since odour dispersion modeling is mainly concerned with the near-field concentrations (within 1,000 m of the source), short-range models are favoured over long-range models.

3.2.4.2 Factors that Affect Dispersion

All dispersion models account for the main factors that affect the movement and diffusion of particles in the atmosphere. These factors include weather stability and wind speed, strength and variability of the emission source, and the physical characteristics of the emission source (height, velocity and temperature of gas stream, etc.) Most models include modules or algorithms to include the effects of topography and building

downwash while some models deal with specific types of emission sources (point, line, area, or volume sources). It is essential that the users of the models understand the impacts of each of these effects on the dispersion process in order to properly interpret the results (Ministry for the Environment, 2000).

3.2.4.3 Challenges of Dispersion Modeling

While research has shown that atmospheric dispersion models are suitable for odour dispersion modeling, it remains a challenge to correctly apply the models to accurately predict downwind concentrations and determine appropriate separation distances. Problems associated with odour modeling include the high uncertainty in odour intensity measurements by human assessors, the variability in protocols for odour emission measurements, the uncertainty in the odour concentration and intensity conversion equation, and the uncertainty in using time-averaged odour data. Additionally, particulate dispersion models are based on the mass of the particulate. Uncertainty in estimation of the mass of odour and the potential physio-chemical change in odour over time make the application of these models problematic.

Current research has largely focussed on validating dispersion models for use with livestock barns and manure storages (Xing et al., 2006). Additional problems arise when attempting to model emissions from activities such as the land application of manure. Manure-applied fields are a large, ground-level area source and the emission strength is spatially and temporally variable. Most likely, this type of situation would need to be idealized in order to be modeled, and a combination of several models with specialized modules would be required to accurately predict the downwind concentration of odour. However, factors that are a major concern with buildings and storages (i.e. building downwash) should not be an issue with modelling emissions from manure application.

3.2.5 Identification of Research Gaps and Objectives

Based on the review of literature, the methodology for odour sample collection from manure application sites has not been well defined. Since manure spreading has been identified as an activity where odour reducing technologies may be successfully applied, baseline data on odour emissions from varying manure types and application methods are required to properly assess the effectiveness of odour reducing technologies. There have been few studies that comprehensively compared the odour emissions from liquid and solid manure at varying application rates and even fewer that compared the effects of injection or sub-surface application on odour emissions.

Intensive livestock regulators would like to establish science-based set back distances for production buildings, manure storages and manure spreading activities. However, odour dispersion modeling for manure spreading is a challenging task that requires knowledge of the odour emission rate variation over time after application of manure. It is likely that the type of manure and method of application will affect not only the magnitude of the emission rate but also the trend of the variation over time, neither of which have been previously investigated.

Based on the identification of these research gaps, the objectives of this research are:

- to evaluate existing equipment and protocols for odour emission determination following land application of manures and, if required, develop new protocols and equipment for sample collection,
- to evaluate the relative odour emissions from various types of solid and liquid manure with both surface and sub-surface application, and
- to develop and validate mechanistic models for the prediction of odour volatilization following land application of liquid and solid manure.

There are many challenges associated with odour emission measurement from land application of manure. These challenges include the varying chemical composition of the manure between and within species, the difficulty in assessing actual field application

rates for full-scale field measurements, ensuring that representative samples are collected from the chambers, and varying background emissions from wet and dry agricultural soil. Lau et al. (2003) noted that odour concentration values collected by chambers also depend on factors such as induced airflow across the enclosure, amount of manure applied and ground surface area covered. In order to draw valuable conclusions related to the emissions from manure application, every attempt should be made to address and/or minimize these factors.

3.3 Materials and Methods

3.3.1 Selection of Measurement and Collection Techniques

Although odour intensity, duration and frequency were identified as key odour indices related to odours from manure spreading, odour concentration offers the ability to calculate an emission rate and make statistical inferences among treatments. Therefore, triangular, forced choice dynamic dilution olfactometry (conforming to CEN (2003) standards) at the University of Alberta was used to analyze air samples for odour concentration (OU/m^3) and hedonic tone. All samples were analyzed within 24 hours of collection.

The literature review (Section 3.2.1) identified the wind tunnel as the preferred method of collecting odour emissions from an area source. However, preliminary testing of a wind tunnel showed that the use of typical wind speeds diluted the samples beyond the measuring capabilities of the olfactometer. Odours from a large area source, such as a field, are initially much more dilute than concentrated area sources such as a manure storage so the method to collect emissions from a manure storage may not be practical for use in a field. Navaratnasamy et al. (2005) also reported that the odour concentration of samples collected using a wind tunnel from a swine manure storage was too low to differentiate from the background odour in the sample bags. Frechen et al. (2004) reported the same problem using wind tunnel technology. Results from the study reported

in Navaratnasamy et al. (2005) suggested that the odour concentration (OU/m^3) could be measured with relatively more confidence using a dynamic chamber than with a wind tunnel.

Also, since the objective of the study was to compare emissions between solid and liquid manure and surface and sub-surface application, absolute or "true" odour emission readings were not necessary. As indicated in the literature review, the dynamic chamber can provide consistent and reproducible comparisons among multiple treatments. The conclusions drawn from such comparisons will be valid and valuable although the resulting data may not be directly comparable to other odour research utilizing wind tunnels.

3.3.2 Measurement of Odour Emissions Using a Dynamic Chamber

3.3.2.1 Description of the Dynamic Chamber

The dynamic chamber used in Navaratnasamy et al. (2005) was designed to have the same surface area dimensions as a standard wind tunnel. This same chamber design was utilized in this study and is shown in Figure 3.1. The chamber was designed and built at the Alberta Agricultural Research Station in Lethbridge, AB. The stainless steel collar (0.8 x 0.4 x 0.1 m) was designed to be placed on the emitting soil to form a good seal and the chamber (0.8 x 0.4 x 0.3 m) to be sealed to the collar with a Styrofoam gasket and clamps. The chamber had a port for incoming air and an exhaust tube that included a sampling manifold. All tubing on the dynamic chamber was made of Teflon to minimize odour contamination of the samples.

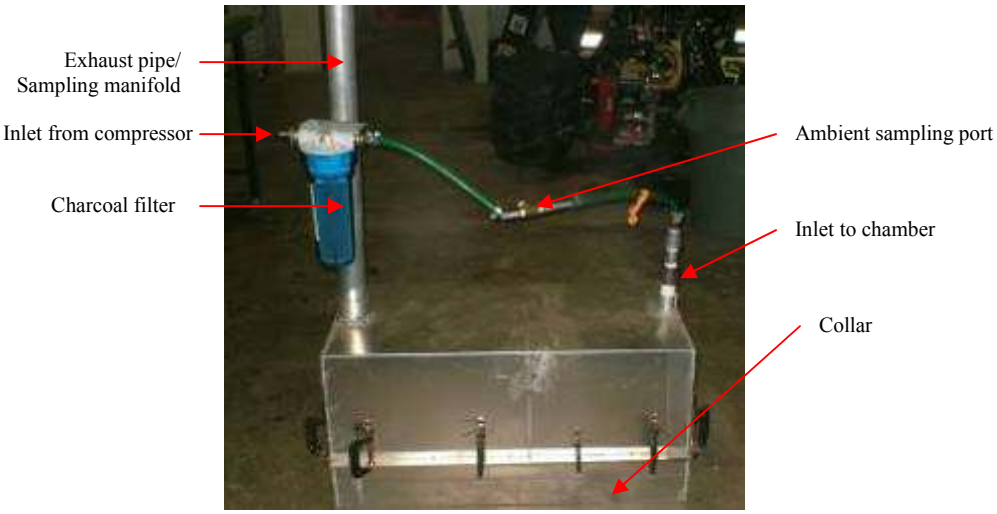


Figure 3.1 Dynamic chamber for odour emission measurement.

3.3.2.2 Optimization of Flow Rate with CO_2 Source

The optimal volumetric flow rate for use in dynamic chambers used for odour measurement from manure application is not well defined in the literature. Researchers have used flow rates ranging from 0.167 to 1.0 L/s for varying designs of chambers. Selecting a low flow rate would result in improper mixing and suppression of emission within the chamber while selecting a high flow rate would excessively dilute the sample. The size and shape of the chamber would also influence the flow behaviour at the soil surface, so each chamber design requires a specific flow rate.

In order to determine the performance of two different dynamic chambers (the rectangular chamber used in this study and a circular chamber used in previous work (Agnew et al., 2005)), a "flux simulation box" was designed and built to supply the chambers with a known flux of CO_2. Since odour is difficult to simulate and measure, using odour tracers was considered impractical. Detailed information on the optimization of flow rate study can be found in Appendix A.

The chambers were operated at a range of flow rates, from 0.236 to 1.888 L/s (0.5 – 4 cfm) and samples were collected from the flux simulation box and each of the chambers. The flux from the box (the "actual flux") ranged from 0.25 – 2.5 mg CO_2/m^2-s and was

compared to the flux collected in each of the chambers. Both chambers performed well at 0.944 L/s (2 cfm or 56.6 L/min). Lower flow rates produced erratic results (the error between the chamber flux and the actual flux was over 80%) while the highest flow rate diluted the sample concentration to background levels. At a flow rate of 0.944 L/s, the error between the measured and actual flux was between 20 and 50%.

While an initial objective of the optimization study was to establish a calibration curve for the chamber, it was discovered that varying environmental conditions (temperature, barometric pressure, soil moisture content, ambient CO_2 concentration, etc.) influenced the chamber performance slightly (refer to Table A.1 in Appendix A), so a calibration curve would need to be developed for each set of environmental conditions. This was deemed impractical for this study.

3.3.2.3 Operation of Dynamic Chamber

During sample collection, the dynamic chamber was deployed on even ground at the sampling site and the collar was pushed into the soil approximately 5 cm to form a good seal. Fresh air was supplied from a portable gas powered air compressor and passed through a rotameter for airflow rate adjustment and a charcoal air filter to remove background contaminants. This sweep air (2 cfm or 0.944 L/s) was allowed to circulate in the chamber for at least 5 minutes before drawing the sample from the sampling manifold. Samples were drawn through Teflon tubing into Tedlar bags with a vacuum box utilizing the sampling lung principle to prevent contamination of the odour sample. The bags were first purged with sample air during the 5 minute equilibration waiting period. The samples were analyzed within 24 hours of collection for odour concentration (OU/m^3) and hedonic tone using olfactometry.

Generally, emissions from dynamic chambers are calculated using Equation 3.1. In the case of odour emissions, the sample had an odour concentration with units of OU/m^3. Also, the odour concentration of the filtered air entering the chamber was assumed to be negligible. Therefore, for the calculation of odour emission from dynamic chambers, Equation 3.4 was used.

$$E = OC * \frac{Q}{A} \tag{3.4}$$

Where E = odour flux (OU/m^2-s),

OC = odour concentration of sample (OU/m^3),

Q = flow rate in chamber (m^3/s), and

A = soil area enclosed by chamber (m^2).

Since uncertainty in odour concentration measurement is inherently high, the percent error in odour flux calculation as determined by Equation 3.4 was about 28% (refer to Appendix C). In addition, odour flux values from a dynamic chamber may not be directly comparable to values calculated using wind tunnel data due to the difference in flow rates used. Since the goal of this research was not to generate odour flux values but, rather, relative comparisons of emissions from different treatments, the majority of the data are analyzed and presented as odour concentration rather than odour flux. Odour fluxes are reported in Tables B.1.and B.3 in Appendix B.

3.3.3 Experimental Design for Data Collection

Odour emissions from surface and subsurface application of liquid and solid manure were measured on a plot scale rather than full-scale field testing to control variables such as application rate and application method and type of manure. Liquid swine and dairy manure and solid swine, poultry and feedlot manure were surface applied and injected at three application rates with 3 repetitions. Application rates were selected based on recommended agronomic rates defined by the nitrogen content of the manure. A recommended "one-year" application rate (1X) would be applied annually to supply enough nitrogen for one year of crop growth. Two and three year application rates (2X and 3X), where larger quantities of manure are applied every two or three years, are common in the Canadian Prairies and were also used in this study. In some cases, full-sized application equipment (i.e.: a liquid tanker injection truck and a solid prototype applicator) were used to apply the manure. Due to the logistical restrictions of the

olfactometer lab, application equipment and land availability, simulated manure application as described below was used in some of the experiments.

The experimental design for all sites was a completely randomized block design to account for soil variability at each site. A summary of the sites used in this study is shown in Table 3.2. For the Muenster location, manure was machine applied by the PAMI liquid manure injector tanker. Each block (repetition) contained 2 species of liquid manure, 2 modes of application and 3 application rates for the surface applied plots and 4 application rates for the injected plots. Samples were also collected from 3 control plots (2 were undisturbed and 1 was disturbed to investigate the effect of soil disturbance on odour emissions).

For the U of S Feedlot and Saskatoon area locations, manure application was simulated by hand. Each block (repetition) included two types of manure, two modes of application and four application rates, including a control rate of zero. Two sets of simulated application experiments were completed in 2007. One set utilized liquid dairy and solid feedlot manure and the other included liquid swine and solid swine manure.
For the Humboldt area location, manure was machine applied by the PAMI prototype solid manure injector. Each block (repetition) included one type of manure, 2 application methods and 4 application rates, including a control rate of zero.

Table 3.2. Summary of odour emission experiments conducted in 2006 and 2007. All experiments were randomized block designs and included surface and subsurface applications at several application rates.

Year	Location	Type of manure	Method of application
2006	Muenster	Liquid swine and liquid dairy	PAMI tanker truck
2007	U of S Feedlot	Liquid dairy and solid feedlot	Simulated application
2007	Saskatoon area	Liquid swine and solid swine	Simulated application
2007	Humboldt area	Solid poultry	Solid injection prototype

Number of odour samples collected (not including samples that were "lost in transit"):
2006: 42 odour samples (all from machine application)
2007: 118 odour samples (94 from simulated application, 24 from machine application)

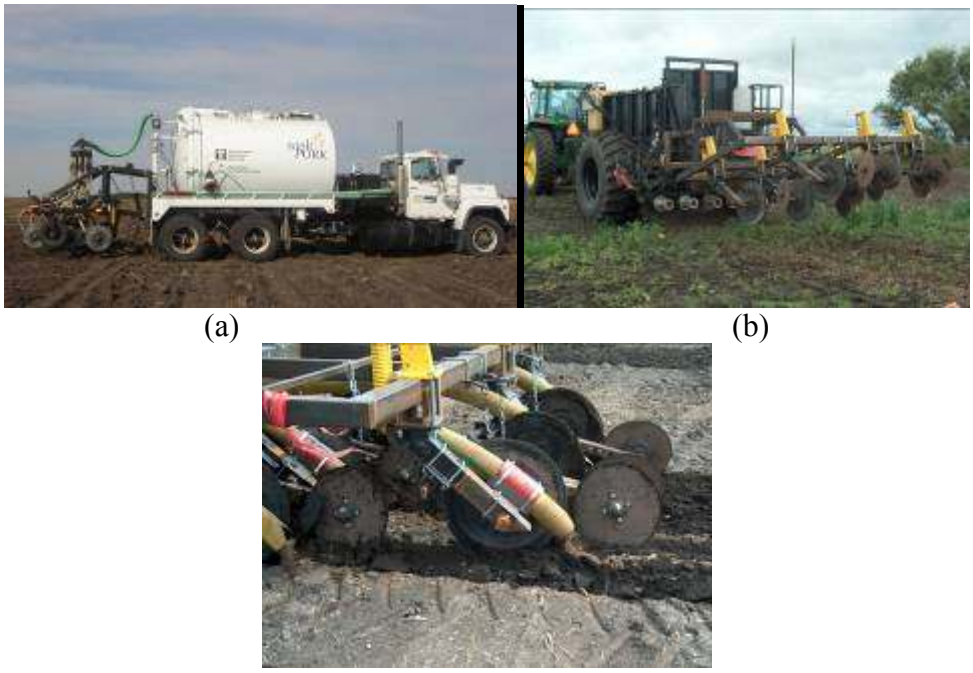
3.3.4 Manure Application

3.3.4.1 Machine Application

The Muenster plots utilizing the PAMI liquid injector tanker truck (Figure 3.2a) were 10 m long and 3 m wide with 3 m spacing between plots. Liquid dairy and swine manure was applied along the entire 10-m length and measurements were taken at random spots in the middle of the plot (to ensure the target application rate had been reached). The flux chamber was deployed within 20 minutes of application. For the injected plots, manure was injected to a depth of 7.5 to 10 cm. The chamber covered 2 furrows for the injected plots.

The target application rates were chosen to simulate typical one-year and two-year application rates based on the nitrogen content of the manure. Since ammonia losses due to volatilization are approximately 60% lower for injected manure (Sommer and Hutchings, 2001), the injected application rates were reduced by 60% so the amount of N retained in the soil would be approximately the same for both application methods (refer to Table 3.3). Due to limitations of the achievable application rate, additional rates of one half and one quarter of one year rates were also used (surface applied manure at a 2 year rate was not feasible). The liquid manure application rates for the plot trial are outlined in Table 3.3 and the chemical properties of the manure used in these plots are in Table 3.4.

The plots utilizing the solid manure injector prototype in the Humboldt trials (Figure 3.2b and 3.2c) were 10 m long and 3 m wide with no spacing between plots. Poultry manure was both surface-applied and injected to a depth of 7.5 to 10 cm. The dynamic chamber was deployed near the center of the plot within 10 minutes of application. For the injected plots, because the row spacing was 40 cm, the chamber covered only one furrow. The poultry manure application rates were the same as those used for the solid manure simulated application plots (Table 3.5) and the chemical properties of the poultry manure are listed in Table 3.6.



(a) (b)

(c)

Figure 3.2 Machine manure applications a) PAMI's liquid manure injector tanker truck b) solid manure injection prototype (broadcast mode) c) solid manure injection prototype (injection mode).

Table 3.3. Liquid manure application rates for PAMI injector truck plots (Muenster).

	Dairy (m^3/ha)		Swine (m^3/ha)	
Rate	**Surface**	**Injected**	**Surface**	**Injected**
0.25X	21	8	23	9
0.5X	42	17	47	18
1X	84	34	94	37
2X	n/a	68	n/a	75

Table 3.4. Liquid manure chemical properties for PAMI injector truck plots (Muenster).

	Total Solids (%)	Ammonia as N (kg/m^3)	Total N (kg/m^3)
Swine manure	2.0	2.99	3.46
Dairy manure	7.0	2.03	3.58

3.3.4.2 Simulated Application

Another set of smaller plots (2 m x 1 m) utilized simulated manure application of liquid and solid manure. The application rates were calculated based on the area of the plot and the volume and mass of liquid and solid manure, respectively, required to simulate typical application rates. For these plots, the application rates for surface and injected applications were equivalent. The application rates simulated in these plot trials are

outlined in Table 3.5 and the chemical properties of the manure used in these plots are in Table 3.6.

Table 3.5. Liquid and solid manure application rates for simulated application plots.

Rate	Solid (Mg/ha)	Liquid (m^3/ha)
1X	20.2	56.1
2X	40.4	84.2
3X	60.6	112.2

Table 3.6. Manure chemical properties used in simulated application plots.

	Total Solids (%)	Ammonia as N (kg/m^3)	Total N
Solid feedlot	38.2	n/a	8.3 kg/Mg
Liquid dairy	6.9	0.60*	2.5 kg/m^3
Solid swine	43.2	n/a	7.0 kg/Mg
Liquid swine	2.8	2.88	3.24 kg/m^3
Solid poultry**	46.4	3.25	17.3 kg/Mg

*Liquid dairy manure was "generated" by taking fresh semi-solid manure directly from alley of barn and diluted with equal parts of water, and applied within 12 hours of mixing, resulting in little time for microbial activity and generation of NH_4-N.
**Solid poultry used for machine application only.

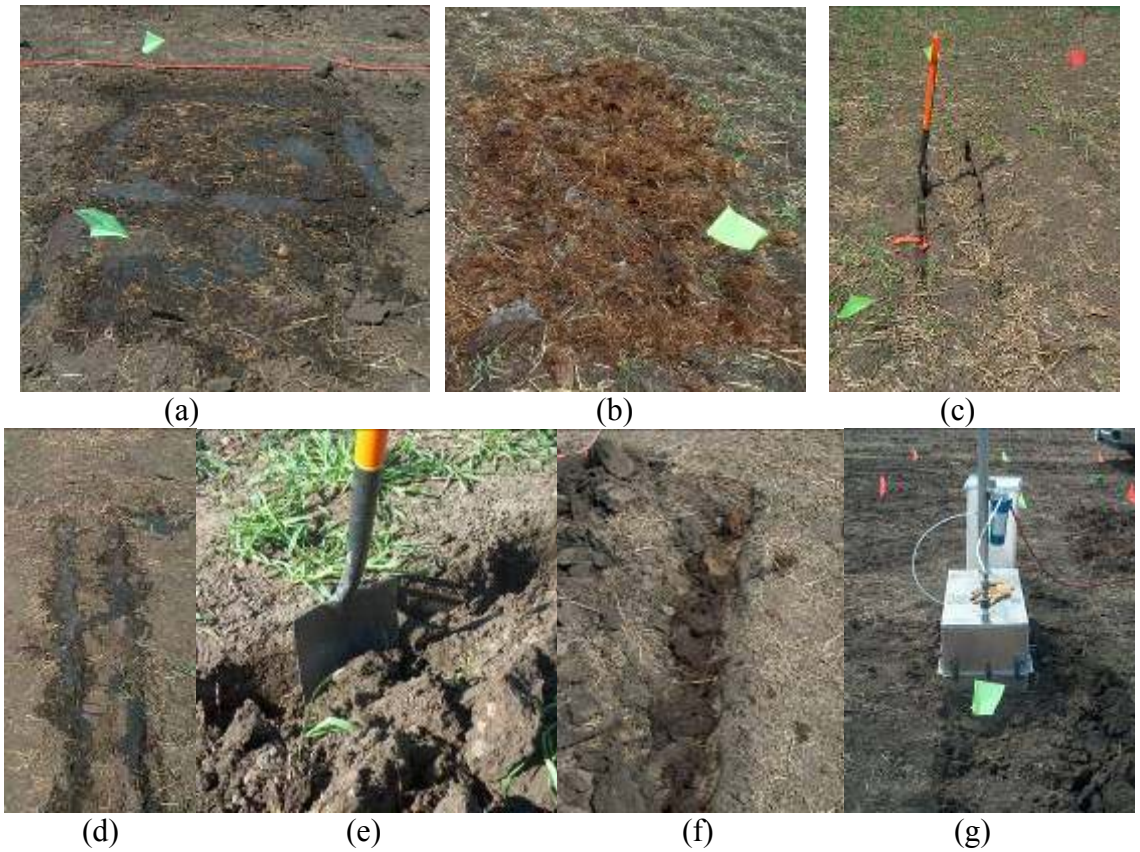


Figure 3.3 Simulated manure applications a) Liquid swine manure surface application (3X rate) b) Solid feedlot manure surface application (3X rate) c) Liquid injection furrows d) Liquid injection (2X rate) e) Solid injection furrow f) Solid injection (2X rate before covering) g) Solid injection odour measurement (2X rate after covering).

For liquid surface application, the manure was poured from a bucket over a 10 cm diameter "splash plate" about 30 cm above the surface of the ground and covered the entire plot (Figure 3.3a). For solid surface application, the pre-weighed manure was simply forked over each plot (Figure 3.3b). For liquid injection, two furrows were cut into each plot 30 cm apart to a depth of 7.5 cm using a square spade (see Figure 3.3c) to simulate liquid injection achieved by the equipment used for machine application. The liquid manure was then poured through a pail spout evenly into each furrow (Figure 3.3d).

To simulate solid injection, a single furrow was cut into the soil using the spade. Because solid injection results in more soil disturbance than liquid injection, the furrows for the solid injection were wider and the depth varied between 7 and 10 cm (see Figure 3.3e). Also, because the injector prototype spacing was 40 cm, the chambers could only accommodate one furrow. The amount of manure applied to each plot was adjusted to accommodate the effective plot size of the injected plots. Solid manure injection for the 2X application rate is pictured in Figure 3.3f (before covering) and 3.3g (after covering and with the flux chamber).

3.3.5 Soil Properties

The three sites (U of S Feedlot, Saskatoon area and Humboldt area) used for the experimental plots in 2007 were all in the dark brown chernozemic soil region of Saskatchewan. Individual soil properties for the three sites are listed in Table 3.7. The moisture content was assessed using the gravimetric oven dry method (104°C for 24 h) and the bulk density approximation was based on published values for the texture class. The nitrogen, organic carbon and organic matter contents were analyzed by ALS Laboratory Group in Saskatoon, SK using standards outlined in Nelson and Sommers (1996) and Tiessen and Moir (1993). The Muenster site (2006 odour data) was also a dark brown chernozemic soil, but additional soil properties were not analyzed.

Table 3.7. Soil properties for data collection sites.

Site Location	Texture Class	Moisture Content Range (% d.b.)	Bulk Density (g/cm^3)	Nitrogen Content (% LECO-N)	Organic Carbon Content (%)	Organic Matter Content (%)
U of S Feedlot	Sandy loam	15.7 – 34.4	1.49	0.30	3.2	5.5
Saskatoon area	Loam	19.8 – 23.8	1.47	0.34	3.4	5.8
Humboldt	Clay loam	26.1 – 31.9	1.31	0.44	4.4	7.5

3.3.6 Statistical Analysis

Humans are considered to respond logarithmically to odour concentration (Qu et al., 2010) so calculations and statistical analyses on odour results were performed on the logarithm of the OU value. Based on a Kolmogorov-Smirnoff test (Greenberg, 2006), the log OU data were very close to being normally distributed so statistical analyses of the hedonic tone and log OU (odour concentration) were completed using Minitab v.15 and the General Linear Model procedure (Greenberg, 2006). Treatments were considered to have a significant effect on the result when the P value was less than 0.05 (95% level of confidence).

Outliers, or infrequent observations, can cause problems in statistical analysis. Generally, if a measurement is greater than 2 standard deviations from the mean of all observations, it may be treated as an outlier and omitted from the data set. However, because odour data are highly variable, this standard may be impractical and result in many outliers. Therefore, for odour data to be treated as outliers, it was assumed that they must be greater than three standard deviations from the mean of all observations

Low odour emissions or concentrations can also affect the results of the statistical analysis. Other researchers have stated that background odour concentrations in the Tedlar bags used to transport odour samples can be as high as 50 to 150 OU/m^3 (Moseley et al., 1998; Qu and Feddes, 2006). Therefore, results less than 150 OU/m^3 can

theoretically be treated as zero since it would be impossible for the odour panellists to differentiate between the background in the bag and odour in the actual sample.

3.4 Results

Due to the differences among application rates and methods of application between the 2006 and 2007 odour data, the results were analyzed independently and will be presented separately. Tables B.1 and B.3 in Appendix B include numeric summaries of log OU, hedonic tone and odour emission rate data with and without outliers. Table B.4 is a numeric summary of all odour concentration and log OU data collected in this study. Figures B.1 to B.6 in Appendix B include additional graphical summaries of the odour concentration data from this study (without outliers). Appendix C includes an uncertainty analysis for the odour emission rate calculation (Equation 3.4).

3.4.1 Data from 2006 Experiments

3.4.1.1 Outliers

Table B.2 (in Appendix B) identifies the outliers and the rationale behind their exclusion. For the 2006 odour data, one data point was identified as an outlier: rep 2 from the 1X surface application of liquid dairy manure. All statistical analyses reported in this section were completed on the data set excluding this outlier. There were no odour samples less than 150 OU/m^3 in the 2006 data.

3.4.1.2 Effect of Manure Species, Application Method and Application Rate

For the 2006 odour data, the odours from swine manure were significantly higher than from dairy manure (P=0.000) and odours from the injected plots were significantly lower than from the surface applied plots (P=0.002). In the 2006 data set, injection significantly lowered odours from both the swine and dairy manures. However, there were no statistical differences among application rates (P=0.545), indicating odours from the

manured plots were not distinguishable from odours from the control plots. This was due to the lack of data from control plots during the 2006 experiment, resulting in a high variation of odour for the 0X application rate. In addition, the 2X application rate was injected only, resulting in lower odours from the 2X rate.

A graphical summary of the log OU data is presented in Figure 3.4 (numeric summary in Tables B.1 and B.3 in Appendix B). Additional graphical and numerical summaries showing the effect of application method and rate on odour concentrations are shown in Appendix B.

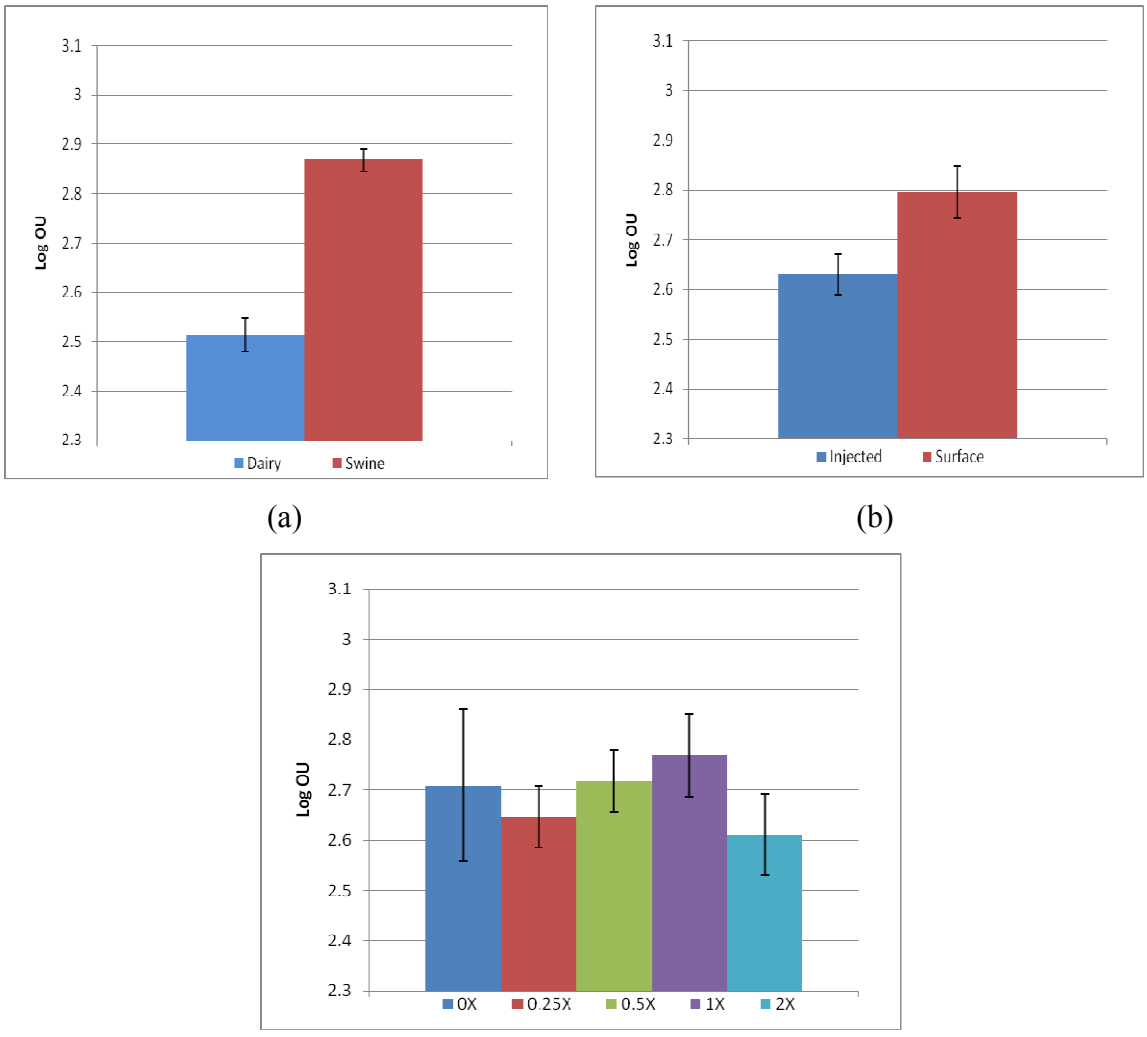


Figure 3.4 Graphical summary of 2006 odour data (log OU), a) Effect of manure species, b) effect of application mode, and c) effect of application rate. Error bars represent the standard error of the mean.

3.4.1.3 Specific Odour Emission Rate (OU per kg N per s)

To determine the effect of application rate on odour emissions, three application rates were chosen based on preliminary analyses of the nitrogen content of the manure. Due to limitations of the equipment used to apply the manure in 2006, surface applications in excess of 95 m^3/ha (10,000 gal/acre) were not possible. Therefore, additional rates were calculated by dividing the one year rate by two and four. In addition, for the 2006 plots, the application rates were adjusted for the injected treatments since losses of N due to volatilization are lower for injected manure (Sommer and Hutchings, 2001). After the final analyses of the nitrogen content of the manure were available, the actual N application rates for the plot trials were calculated. A summary of the actual application rates of total N and NH_4-N for the different rates and application methods used in the 2006 plots are shown in Table 3.8.

Table 3.8. Summary of actual N application rates for 2006 plot trials.

			kg N-tot/ha			kg NH_4-N/ha		
	Total N kg/m^3	**NH_4-N kg/m^3**	**0.25X**	**0.5X**	**1X**	**0.25X**	**0.5X**	**1X**
Swine (Surf)	3.5	3.0	80	163	326	69	141	281
Swine (Inj)	3.5	3.0	31	62	128	27	54	111
Dairy (Surf)	3.6	2.0	75	150	301	43	85	170
Dairy (Inj)	3.6	2.0	29	57	114	16	35	69

Since the actual application rates based on N content of the manure were not the same for both manure species, specific odour rates were calculated by dividing the odour emission rate by the total N application rate. The resulting odour rates ("N specific odour flux") have units of OU/kg-N-s and allowed better comparisons among manure types.

The specific odour fluxes for the 2006 data are shown in Figure 3.5. Specific odour fluxes from swine manure applications are still significantly higher than from dairy applications. However, based on the 2006 specific odour flux data, injecting manure actually increases specific odour emissions. The magnitudes of the odour emissions from the injected plots were indeed lower than the surface plots, but this was mainly due to the lower application rate rather than reduced volatilization and/or diffusion of odour compounds. Also, the specific odour decreased with application rate, suggesting that the proportion of manure compounds that volatilize decreases with application rate. This is

probably due to the solid manure "piling" and the liquid manure "ponding" at higher application rates, limiting the surface area in contact with the air and limiting volatilization.

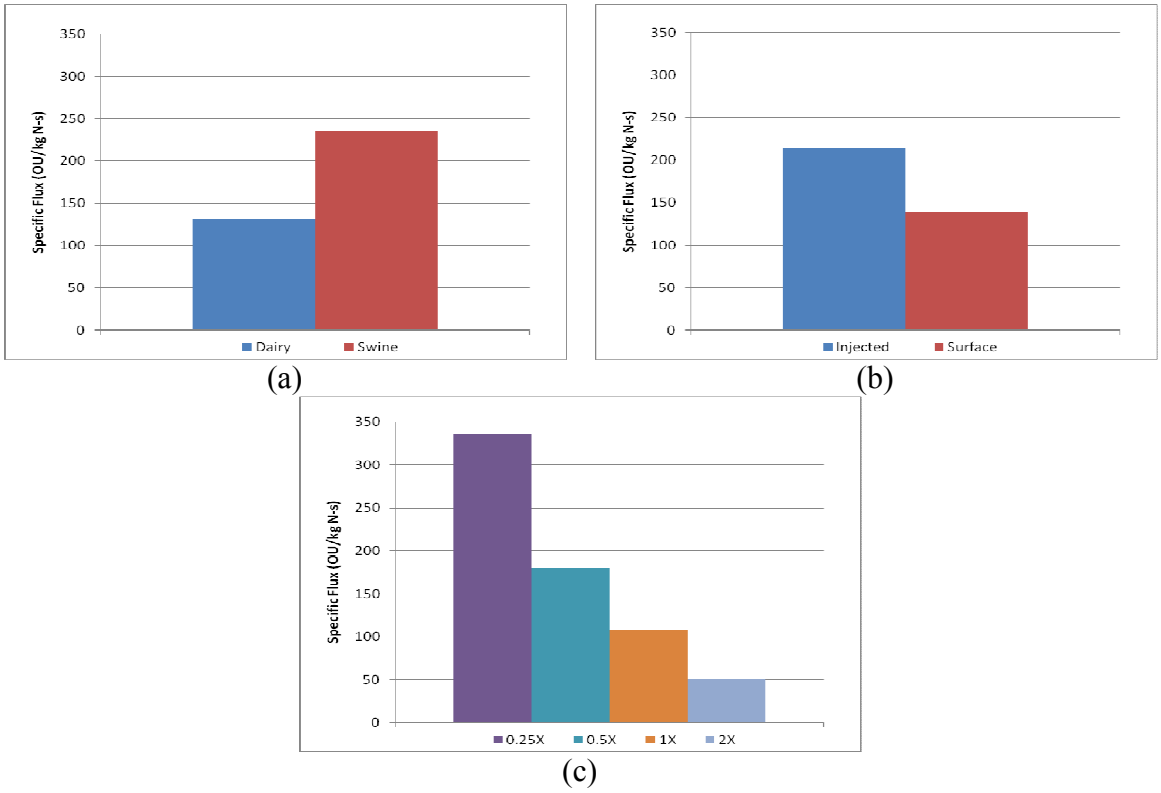


Figure 3.5. Specific odour rate (OU/kg N-tot-s) for 2006 plot trials, a) effect of manure species, b) effect of application mode, and c) effect of application rate.

Specific odour rates in terms of kg NH_4 applied were also calculated and analyzed, but the trends were very similar to those calculated in terms of kg N-total. Additional graphs showing the effect of manure type, application method and application rate on specific odour rates are shown in Appendix B.

3.4.2 Results from 2007

3.4.2.1 Outliers

Table B.2 identifies the outliers and the rationale behind their exclusion. For the 2007 odour data, 2 data points were identified as outliers: repetitions 1 and 2 from the 3X

injection of liquid swine manure. All statistical analyses reported in this section were completed on the data set excluding outliers.

Several of the control plots from 2007 returned odour concentrations less than 150 OU/m^3. In addition, nearly all of the solid swine injected plots (all rates, all reps except 2X-3) returned odour concentrations less than 150 OU/m^3. This indicates that the odour from the solid swine injected plots was not distinguishable from the background odour in the Tedlar bags. Even so, these data were not omitted from the data set.

3.4.2.2 Effect of Manure Species, Application Method and Application Rate

For the 2007 odour data, results at the 95% level of confidence indicated that odours from liquid manure application were significantly higher than odours from solid manure application (P=0.001) and odours from the 1X, 2X and 3X application rates were statistically higher than odours from the control plots (P=0.000). When the two 2007 outliers were excluded, the odour emissions from the injected treatments were significantly lower than emissions from the surface applied treatments (P=0.002).

When examined individually, injection significantly decreased odour emissions from liquid dairy manure (P=0.000) and solid swine manure (P=0.000) (see Figure B.5b in Appendix B). The odours from the solid feedlot manure were too low to determine a statistical trend (P=0.274) while the odours from the poultry manure plots were too variable to determine a statistical trend (P=0.196). Alternatively, injection of the liquid swine manure actually significantly increased odour emissions (P=0.002), even when the two outliers were omitted. A graphical summary of the log OU data is presented in Figure 3.6 (numeric summary in Tables B.1 and B.3 in Appendix B). Additional graphical and numeric summaries showing the effect of application method and rate on solid manure and liquid manure separately are shown in Appendix B.

The effects of treatment interactions were assessed for the 2007 odour data only. The P values for the type*mode, type*rate, mode*rate and type*mode*rate interactions were

0.066, 0.031, 0.251 and 0.541, respectively. Therefore, only type*rate interaction was significant at the 95% level of confidence. These interactions are plotted in Figure B.8 in Appendix B. The type*rate interaction indicates that odour concentration increases at a different rate for solid manure than liquid manure. However, this was due to an arbitrary assignment of control plots to either "solid" or "liquid" manure. If the control odours are ignored on the interaction plot, the rate of increase in odour concentration is the same for both manure types.

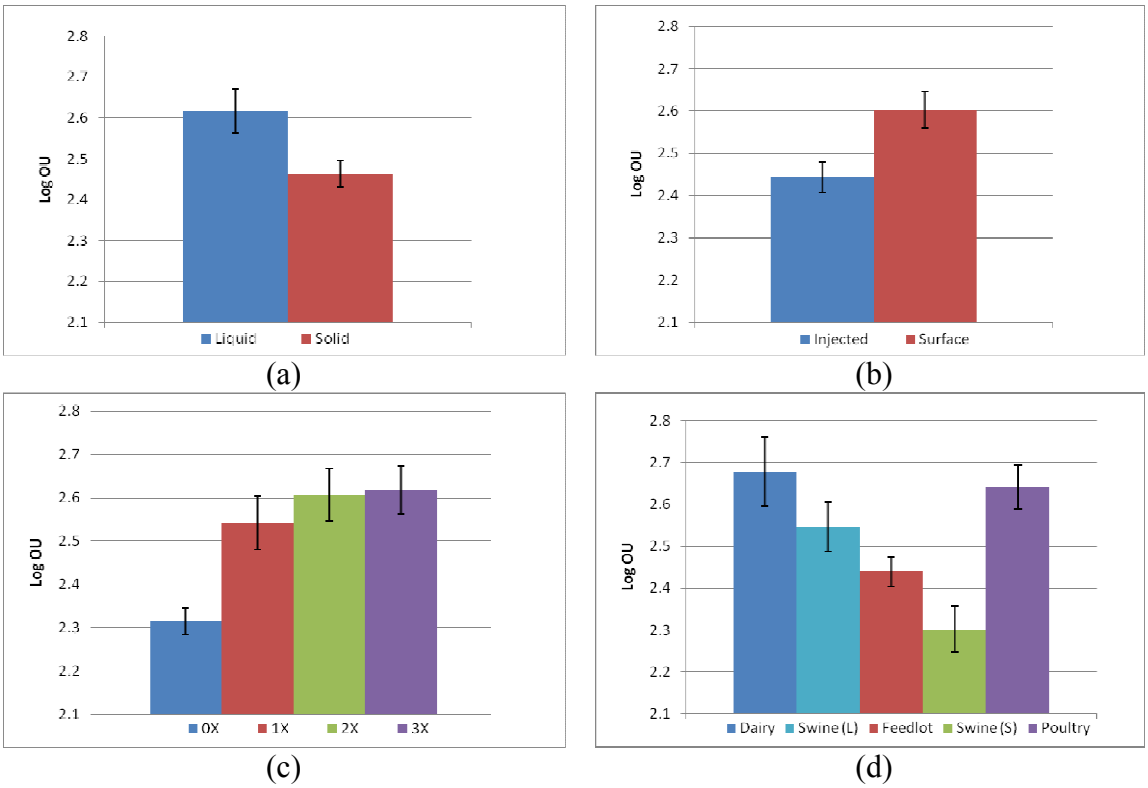
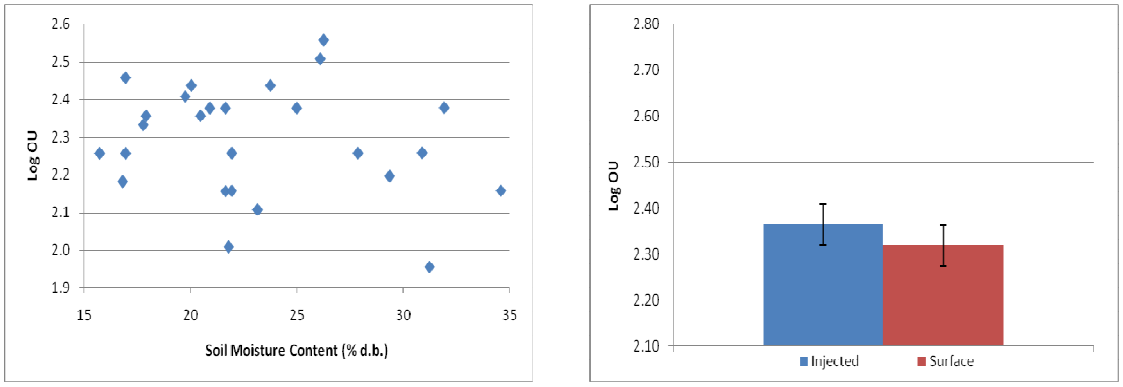


Figure 3.6 Graphical summary of 2007 odour data (log OU), a) effect of manure type, b) effect of application mode, c) effect of application rate, and d) effect of manure species. Error bars represent the standard error of the mean.

3.4.2.3 Control Odours

It was hypothesized that soil moisture content and soil disturbance may affect odour concentration and hedonic tone from samples collected from the experimental plots. To determine whether soil moisture was a factor, the log OU values from the control plots were plotted against soil moisture content in Figure 3.7 (2007 data only). There was no apparent correlation between soil moisture content and odour concentration. Similarly,

there was no correlation between soil moisture content and hedonic tone (Figure B.7 in Appendix B).



(a) (b)

Figure 3.7 Control odours (a) effect of soil moisture (% d.b.) on control (0X) odours, and (b) effect of soil disturbance on control odours. Error bars represent the standard error of the mean.

Some research has suggested that injection of manure may increase odour concentrations since injection results in soil disturbance, contributing to the amount of odour compounds present in the air immediately above the soil surface (Rahman et al., 2004). Comparing the log OU data between the disturbed and undisturbed control plots from the 2007 data shows the disturbed plots had slightly higher odour concentrations than the undisturbed control plots (Figure 3.7b). However, this difference was not statistically significant (P=0.367), suggesting that the soil disturbance resulting from manure injection does not contribute to the overall odour emissions from manure application. Similarly, the hedonic tones were the same for both control treatments.

3.4.2.4 Specific Odour Emission Rate

For the 2007 plot trials, the application rates were set to 100, 300, and 500 kg N/ha respectively based on preliminary analyses of the nitrogen content of the manure. Injected and surface applied plots received the same application rates. After the final analyses of the nitrogen content of the manure were available, the actual application rates for the 2007 plot trials were calculated and are presented in Table 3.9.

The 2007 specific odour rate data are graphically summarized in Figure 3.8. The specific odour rate results showed significant differences for type of manure (P=0.000), mode of application (P=0.016) and application rate (P=0.026). In contrast with the 2006 data, injection did decrease odours compared to surface application. Again, specific odour decreased with application rate due to limited surface area contact with the higher application rates. The specific odour fluxes from the three types of solid manure were similar to each other and were all lower than the specific odour rate from the two liquid manures.

Table 3.9. Summary of actual N application rates for 2007 plot trials.

			kg N_{tot}/ha			kg NH_4-N/ha		
Manure	**Total N**	**NH_4-N**	**1X**	**2X**	**3X**	**1X**	**2X**	**3X**
Feedlot	8.3 kg/Mg	2.1 kg/Mg[1]	168	335	503	42	85	127
Swine (S)	7.0 kg/Mg	1.8 kg/Mg[1]	141	283	424	35	71	106
Poultry	17.3 kg/Mg	3.3 kg/Mg	350	700	1050	66	131	197
Dairy	2.5 kg/m^3	0.60 kg/m^3[2]	140	211	281	34	51	67
Swine (L)	3.2 kg/m^3	2.9 kg/m^3	182	273	364	161	242	323

[1] NH_4-N analysis for the solid feedlot and solid swine manure were not available. Literature values (Webb et al., 2001) state that approximately 25% of total N is in the form of plant available NH_4-N for these types of manure.

[2] Liquid dairy manure was "generated" by taking fresh semi-solid manure directly from alley of barn and diluted with equal parts of water, and applied within 12 hours of mixing, resulting in little time for microbial activity and generation of NH_4-N.

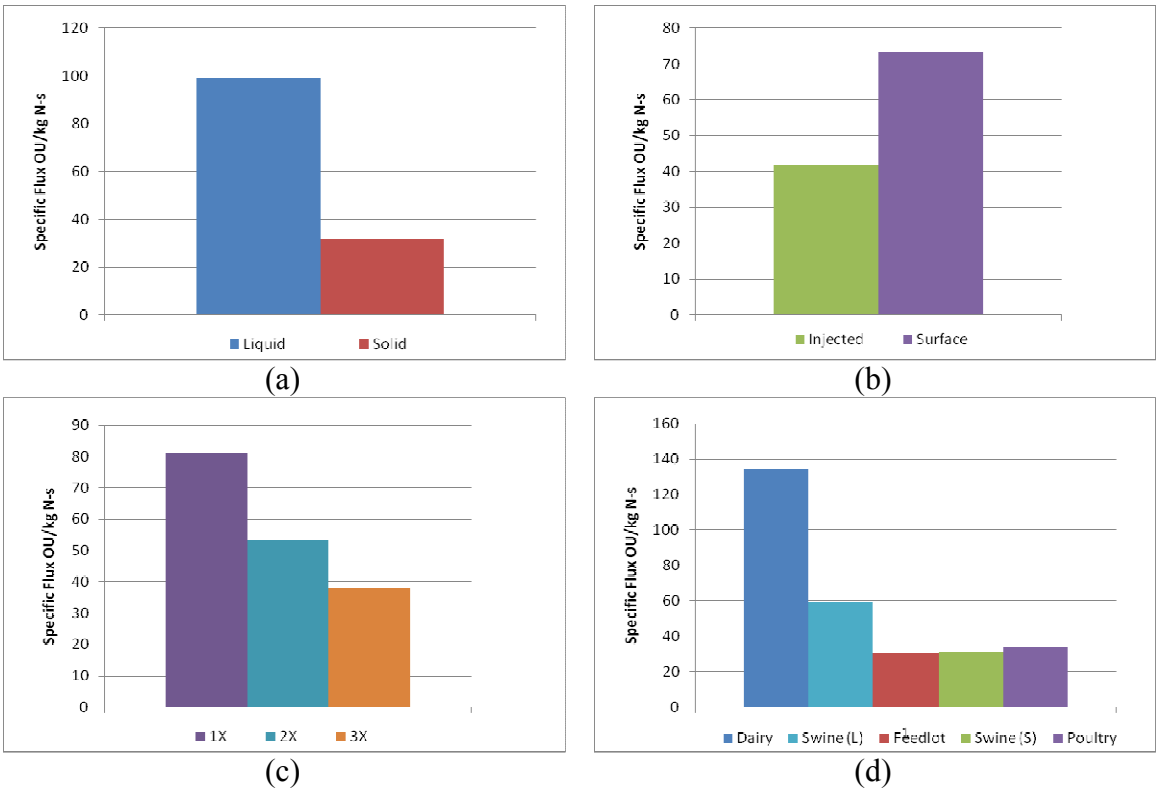


Figure 3.8. Specific odour rate (OU/kg N_{tot}-s) for 2007 plot trials, a) effect of manure type, b) effect of application mode, c) effect of application rate, and d) effect of manure species.

Additional graphs showing the effect of manure type, application method and application rate on specific odour rates are shown in Appendix B.

3.4.2.5 Hedonic Tone

Even though hedonic tone is considered a subjective measure, the results show interesting trends for odours from manure application. For the 2007 data, odour from the solid manure plots were considered more pleasant than odour from the liquid manure plots (P=0.000). Although the odour from the surface application was slightly more pleasant than from the injected applications, this difference was not statistically significant (P=0.502). Not surprisingly, odour from the control plots were significantly more pleasant than odours from the 1X, 2X and 3X application rates (P=0.027). There were no significant differences among hedonic tones for the 2006 odour data.

3.5 Discussion

3.5.1 Comparison Between 2006 and 2007 Data

The 2006 data are not directly comparable to the 2007 data since manure was mechanically applied in 2006 and hand applied in 2007. In addition, the manure sources were different between the two years. The liquid swine and dairy manure used in 2006 were obtained from commercial livestock facilities. In 2007, the dairy manure came from the U of S research barn and was diluted to obtain a similar solids content as 2006, and the liquid swine manure was obtained from a small livestock facility with underground concrete storage tanks (compared to the earthen manure storages in 2006). In the 2006 data set, odours from swine manure were significantly higher than odours from dairy manure while, in 2007, the odours from the swine manure were lower than dairy manure. The liquid swine and liquid dairy data in 2007 were collected at different sites, however, making the comparison between swine and dairy manure difficult due to varying background effects. Additionally, even though the odour samples were analyzed at the

same olfactometry lab in both years, different panellists may have analyzed each set of samples, resulting in different odour concentration values. One other study directly compared odour emissions between liquid swine and dairy manure (Oh et al., 2004). For three application techniques (splash plate, hose spreader, hose spreader + disk harrow), the odour from the swine manure was higher than odour from the dairy manure (Oh et al., 2004). In another study, Pain et al. (1988) showed no difference in the odour emission rate trend over time between separated cattle slurry and pig slurry.

3.5.2 Effect of Application Method on Odours

As expected, odour emissions from injected plots were generally lower than odour emissions from surface applied manure plots. Overall, the odour concentrations from the injected plots were 37% lower than from the surface plots. Injection decreased odour concentrations from solid manure application by 47% while injection decreased odours from liquid manure by 24%. Therefore, injection appeared to reduce odours more effectively and consistently for solid manure than for liquid manure.

When examined individually, injection decreased odours by 62, 27, 46, and 66% for liquid dairy, solid feedlot, solid poultry and solid swine, respectively. For the liquid swine manure, the odours from the injected treatment were actually 136% higher than the surface odours as measured immediately after application. This was probably due to ponding of manure on the surface for the 2X and 3X application rates, resulting in high concentrations of manure on the surface of the soil directly beneath the dynamic chamber. The injection of solid manure by hand and by the prototype resulted in 90 to 100% manure coverage and provided consistently lower odours compared to the surface applied plots. Finally, the two outliers in the 2007 data set were from the liquid swine injection plots (3X), making the adjusted data for the liquid swine injected plots more variable due to lack of data points.

In 2006, injection actually increased the specific odour flux while, in 2007, injected decreased the specific odour flux. To allow a better comparison with the 2006 data, only

the liquid manure results from 2007 were analyzed to determine the effect of application method on specific odour flux. For the 2007 liquid manure specific odour data, the results from the injected plots were lower than from the surface plots, but the difference was not significant (P=0.082). This indicates that injection tends to reduce odours on a per kg N applied basis, but this reduction may not be statistically significant.

Several researchers have concluded that incorporation or "burying" manure during or after application will result in lower odour emissions compared to surface applications (Lindvall et al., 1974; Phillips et al., 1990; Lau et al., 2003; Moseley et al., 1998). Oh et al. (2004) showed that odours from a hose spreader were six times lower than those from a splash plate while Hanna et al. (2000) reported that most incorporation methods (narrow knife, sweep, chisel) reduced odour levels by 20 to 90% from the odour level emitted after broadcast application. Lau et al. (2003) reported a decrease in odours of 8 to 38% between surface and sub-surface deposition. However, Pain et al. (1991) noted that a worthwhile reduction (52%) in total odour over 48 hrs was achieved only by immediate ploughing. No reduction in total emissions was detected when incorporation was delayed for 3 to 6 hrs after slurry application (Pain et al., 1991). The observed percent reduction in odours from injected plots versus surface plots in this study is similar to those reported in literature.

3.5.3 Effect of Manure Type on Odours

The results from this study indicate that odour concentrations from liquid manure were 37% higher than odour concentrations from solid manure. This difference is even higher (68%) when the specific odour fluxes of liquid and solid manure treatments were compared. This suggests that when liquid and solid manure are applied at comparable N rates, the liquid manure will likely generate higher odour emissions.

Of the solid manure species, the poultry manure applications resulted in the highest odour concentrations. However, the amount of N applied per plot was higher for the poultry manure than for the feedlot and solid swine manure because of the high N content of the

poultry manure. When the specific odour fluxes were calculated, odours from the poultry manure applications are equivalent to the solid swine and feedlot manure applications.

The conclusion that odours from liquid manure applications were higher than solid manure applications is valid only for the first 20 minutes after application since all samples were collected within 20 minutes. Smith et al., (2007) monitored odour emissions over a 42 hour period after application and noted that overall odour emissions from liquid manure applications were lower than emissions from solid manure applications. The authors attributed this result to the infiltration capacity of the soil; the liquid manure infiltrated quickly but the solid manure remained on the surface, generating higher emissions for an extended period of time (Smith et al., 2007).

3.5.4 Effect of Application Rate on Odours

Generally, for the 2007 data, odour concentrations from 1X, 2X and 3X application rates were significantly higher than odour concentrations from non-manured plots. While the 2X and 3X application rates generated 10 to 15% higher odour concentrations than the 1X rate, the difference was not statistically significant. This trend was observed for both solid and liquid manure. Injection seemed to be more effective at reducing odour concentrations from the 1X application rate (54% reduction) than the 2X and 3X application rates (33% reductions).

An interesting trend was observed for the effect of application rate on the specific odour data. The specific odour data represents the odour flux per kg N applied. Even though nitrogen compounds such as ammonia are not strongly correlated with odour emission, application rates are often based on N content so the specific odour flux allows comparison among different manure types and application rates. Although the odour concentrations increased with application rate, this increase was not proportional to the increase in amount of N applied. This resulted in a decreasing trend between application rate and specific odour rate (Figures 3.5c and 3.8c). Again, this is explained by the "piling" or "ponding" effect of the manure at higher application rates resulting in less

contact area and volatilization between the manure and the atmosphere. It must be stressed that increasing the application rate is not a viable strategy to reduce odour emissions. This information merely shows that odour concentrations per kg N applied decrease as the application rate increases. These data also confirm that volatilization is likely the dominant mechanism that generates odours from manure spreading.

Smith et al. (2008) and Mkhabela et al. (2007) utilized micrometeorological methods to study the effect of liquid manure application rates on total odour emissions. Although their results were not statistically significant, Mkhabela et al. (2007) concluded that doubling the rate had no effect on odour emissions but tripling the rate increased emissions relative to conventional (1 year) application rates up to 44%. Smith et al. (2007) noted that 2X and 5X application rates generated 22 and 38% more odour, respectively, than 1X application rates. Rahman et al. (2004) used wind tunnels to measure odours from three application rates but found no correlation between odours and application rate.

Pain et al. (1988) compared the emission rate trend over time after application between two application rates (50,000 and 200,000 L/ha). Similar trends were observed for both application rates, the only difference being the magnitude of emissions shortly after application. There was no evidence that odour from higher rates of slurry application were detectable for a longer period (Pain et al., 1988).

3.5.5 Effect of Time after Application on Odours

Although it was not directly studied in this phase of the research, the effect of time after application on odour emissions has been studied in literature (Lau et al., 2003; Misselbrook et al., 1997; Smith et al., 2007; Moseley et al., 1998; Hanna et al., 2000; Pain et al., 1988, 1991). These researchers concluded that odours after manure spreading return to background levels within 24 hrs. Injection or incorporation of the manure tends to decrease this time to as little as 4 hrs after application. Lau et al. (2003) also noted that the difference in odours between surface and sub-surface deposition over time after

application decreased, although odours from surface applications were still up to 25% higher than sub-surface applications 2.5 hrs after spreading. Results in Pain et al. (1991) show similar emission rate trends over time for an unincorporated control, rigid tines, rotary harrow and plough incorporation. The initial magnitudes of emissions are different for each incorporation method, but within 12 hrs they had the same emissions and the trend is very similar from 12 hrs to 48 hrs after application.

The results from the current study suggest that liquid manure may generate higher emissions initially, but the emissions likely return to background levels very quickly while solid manure generates lower emissions initially, but may take longer to return to background levels. Knowledge of the emission rate versus time relationship over the first few hours after application for both solid and liquid manure with surface and subsurface application will be crucial for modelling of odour dispersion and calculating overall odour emissions from application sites.

3.5.6 Comparison of Results with Literature Values

As previously discussed, results from manure odour research are highly variable due to different environmental conditions, manure sources, and sampling and measurement techniques. Reporting of odour data also differs with some researchers quoting odour emission rates as OU/m^3 and others calculating odours per L of slurry applied. In some cases, odour fluxes are reported with units of OU m/s (odour concentration as OU multiplied by wind speed in wind tunnel) instead of OU/m^2-s (odour concentration as OU/m^3 multiplied by wind speed). All these factors make comparisons among results very difficult. In addition, odour emissions measured by micrometeorological or wind tunnel methods are normally considered "true" emission rates whereas odour data collected using flux chambers (as in this study) are valid only for comparison purposes. Nonetheless, a summary of literature values of odour concentrations and emission rates after land application is presented in Table D.1 in Appendix D. The odour concentrations and relative reduction in odours in this study compare well with other studies using wind

tunnels, but the flux rates in literature and this study vary greatly, likely due to collection and calculation methods.

3.6 Conclusions

Dynamic flux chambers were used in this study for surface odour emission measurement. A sweep air flow rate of 0.944 L/s proved to work well for the magnitude of odour emissions arising from manure spreading activities. However, care must be taken to ensure an accurate measurement of the sweep air flow rate as this source of error can significantly increase the error associated with the odour flux measurement (refer to Appendix C). In addition, sweep air flow rates in excess of 0.944 L/s have the potential to dilute the sample beyond measuring capabilities of the olfactometer. Whenever possible, it is recommended to obtain baseline odour emission data to better select an appropriate sweep air flow rate as a rate of 0.944 L/s may also result in suppression of emissions and erroneous results.

The results of the plot studies indicated that odour concentrations from injected plots were up to 37% lower than concentrations from broadcasted applications. Injection seemed to have a larger impact on reducing odours from solid manure than liquid manure. In fact, odours from injected liquid swine manure were actually higher than odours from surface applied liquid swine manure due to ponding of manure on the surface at high application rates. Injection had no effect on the hedonic tone.

Odours from solid manure were 37% lower than from liquid manure. In general, odours from liquid and solid manure increased with higher application rates, but there was little difference among the one, two and three year application rates. For the plots applied with the PAMI truck, the odour concentrations from the swine manure were higher than the concentrations from the dairy manure, but this trend was reversed in the simulated

application plots. The odour from the solid manure applications was considered more pleasant than the odour from the liquid manure applications.

The calculation of a specific odour flux (the odour emission rate as calculated by Equation 3.4 divided by the amount of N applied) resulted in some interesting trends. For the 2006 data, injection actually increased the specific odour rate, meaning that the observed overall reduction in odour concentration was due more to the reduction in application rate than the reduced volatilization of compounds. For the 2007 data, injection decreased both odour concentration and specific odour rate for all manure types except liquid swine. It was also noted that the specific odour rate decreased with higher application rates. This was due to the reduced surface area available for volatilization of compounds with higher application rates. Higher application rates do result in higher overall odour concentrations, but this increase is not proportional to the amount of N applied.

Based on the results from this study, injection of manure is an effective way to reduce the overall odour emissions from manure spreading, particularly for solid manure. However, other factors associated with manure injection, such as the increased power requirement and soil disturbance, as well nutrient transport and greenhouse gas emissions, must be considered when evaluating the overall impact of manure injection versus surface application.

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Appendix A—Use of a Flux Simulation Box to Determine Optimal Flow Rate in Flux Chamber

Note: This work was presented and published in the conference proceedings for the ASAE Sectional Meeting in Brookings, SD in 2005 (Agnew et al., 2005).

Introduction

Since the volumetric flow rate of the sweep air in a dynamic flux chamber for odour measurement from manure application was not well defined in literature, experiments were carried out to determine the optimal flow rate. The performance of two flux chambers was assessed by operating them on a flux simulation chamber based on the design used by Widén and Lindroth (2003).

Materials and Methods

An airtight box with an open top (1.22 m wide, 2.44 m long, 1.22 m high) (4x8x4 feet) was constructed of oak plywood (Figure A.1). Ports in the flux simulation box allowed for instrumentation (carbon dioxide source, pressure barometer, collection tube, gas release valve, and electrical cable). A gas collection tube ran diagonally from the collection port to the opposite corner at the opposite end of the box. Openings were located at even intervals along the tube. The total surface area of all the holes was equivalent to the cross sectional area of the collection tube to ensure that the tube drew air from the inside of the box evenly. The inside of the box was braced with a 50.8 mm (2 inch) round steel bar which could be expanded by means of a threaded steel rod to provide walls with support. Two small air circulation fans were attached to the support rod to ensure good mixing of the air inside the box. The top of the flux simulation box was then covered with coarse and fine wire mesh and two layers of cotton to provide unrestricted airflow through the top of the box. The top of the flux simulation box was large and sturdy enough to allow placement of both flux chambers and a wind tunnel for performance evaluation.

Carbon dioxide gas pumped into the flux simulation box through the gas supply port and gas was continuously drawn from the inside of the box through the collection tube and analyzed for CO_2 concentration using a Guardian Plus Infra-Red Carbon Dioxide Monitor (±2%, 0 to 3,000 ppm). Once the gas concentration inside the box reached the desired level (approximately 2500 ppm), the CO_2 supply was turned off and the

circulating fans inside the box were turned on. The CO_2 then emitted through the surface of the box, simulating gas emission fluxes. The emitting flux could be measured by monitoring the CO_2 concentration inside the box over specific time intervals as indicated in Equation A.1.

Figure A.1. Overall view of flux simulation box (1.22 m wide, 2.44 m long, 1.22 m high) (4 ft x 8 ft x 4 ft), with an open top and no soil. Ports on the front panel are (from left to right): CO_2 supply port, water manometer for monitoring pressure inside box, variable control for circulating fan speed, power bar for supply for fans, CO_2 analyzer, and collection manifold. A gas relief valve was installed at the back of the box.

$$Flux_{box} = \frac{V(C_{t1} - C_{t2})\rho_{CO2}}{A(t_2 - t_1)} \quad \text{(A.1)}$$

Where $Flux_{box}$ = the CO_2 flux emitting from the surface (mg CO_2/m^2-s),

V = the volume of the flux simulation box (2.56 m^3),

C_{t1} = the concentration of the gas in the box at the beginning of the sampling period (ppm),

C_{t2} = the concentration of the gas in the box at the end of the sampling period (ppm),

ρ_{CO2} = the density of CO_2 at ambient temperature and pressure (1.8 kg/m^3),

A = the surface area of the flux simulation box (2.97 m^2), and

$(t_2 - t_1)$ = the sampling time (s).

Both flux chambers were placed on the top of flux simulation box to collect the CO_2 emitting from the simulated surface. The flux chambers were operated at a variety of air

flow rates (0.5, 1, 2, 3, 4 cfm) to determine the effect of chamber flow rate on measured flux. Once the CO_2 flux from the simulation box had reached steady state (approximately 20 minutes after gas injection), the chambers were placed and sealed on the surface and supplied with fresh air through the compressor, rotameter and charcoal air filter. The flux chambers were also allowed to reach steady-state before sampling began (about 20 minutes after starting compressor). Each sampling period was approximately one hour during which approximately 10 to 20 fluxes were measured. The CO_2 concentration in the flux simulation box was measured and recorded at the beginning and end of the sampling period and samples were drawn from the flux chamber into Tedlar bags at even intervals during the sampling period. An ambient air sample was also drawn from the ambient sample port between the charcoal air filter and the chamber inlet midway through the sampling period for ambient CO_2 concentration determination. At the end of the sampling period, the time was recorded and the concentration of the sample drawn from the chamber was measured and recorded. The CO_2 flux measured by the flux chambers was calculated using Equation A.2:

$$Flux_{chamber} = \rho_{CO2}(C_{sample} - C_{ambient})\frac{Q_{chamber}}{A_{chamber}} \quad \text{(A.2)}$$

Where $Flux_{chamber}$ = the CO_2 flux collected by the chamber (mg CO_2/m^2-s),
ρ_{CO2} = the density of CO_2 at ambient temperature and pressure (1.8 kg/m^3),
C_{sample} = the CO_2 concentration of the sample collected from the flux chamber (ppm),
$C_{ambient}$ = the CO_2 concentration of the ambient air (ppm),
$Q_{chamber}$ = the air flow rate supplied to the flux chamber (m^3/s), and
$A_{chamber}$ = the cross sectional area of the flux chamber (0.323 m^2 for the rectangular chamber and 0.28 m^2 for the circular chamber).

Testing was completed on the calibration box in two stages: open top with no soil, and open top with soil. The open top/no soil tests were used to determine if the airflow in the flux chambers affected the CO_2 flux from the calibration box. The open top/with soil tests were used to assess the performance of the chambers under simulated field conditions at the various flow rates.

Results and Discussion

Open Top without Soil

Since it was possible that the airflow in the chamber on top of the calibration box could affect the natural flux of the CO_2 exiting the simulation box, the simulation box flux was measured with no chambers and with both chambers running at the same time at 1, 2, and 3 cfm. As shown in Figure A.2, the best fit lines for each set of data are very similar,

indicating that neither the presence of flow in the chambers nor the magnitude of the flow rate in the chambers affected the CO_2 flux exiting the box.

These tests were also used to establish a sampling protocol. The chambers were allowed to run for at least 20 minutes prior to sampling to ensure steady-state had been reached, and the lines and bags were flushed with sample air for at least 30 seconds before samples were drawn.

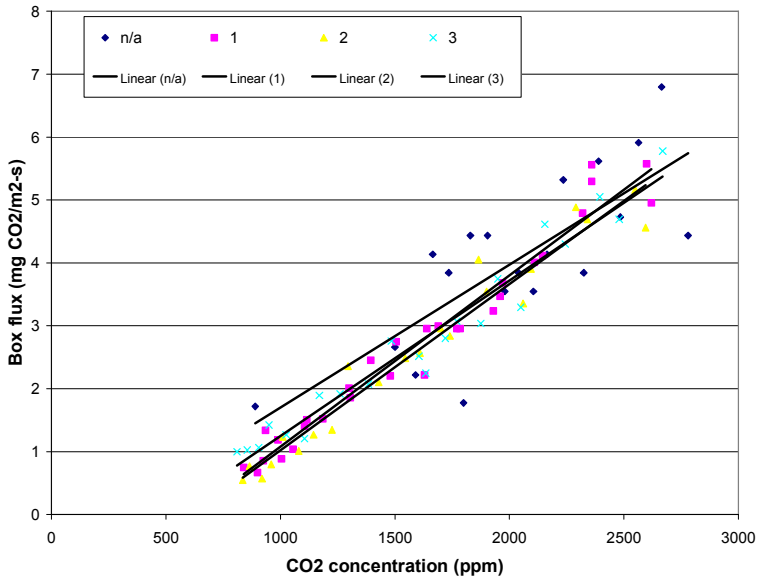


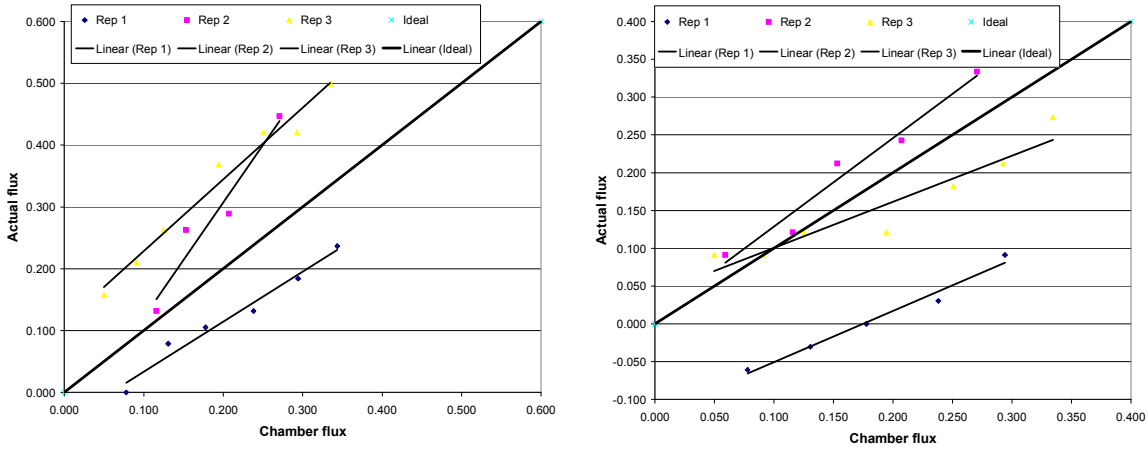
Figure A.2. Effect of chamber flow rate on actual flux with no chamber (n/a), 0.000472 m^3/s (1 cfm), 0.000944 m^3/s (2 cfm), and 0.001416 m^3/s (3 cfm) flow rates in each chamber.

Open Top with Soil

A uniform layer of clay-loam soil 3.5 cm thick was added on top of the calibration box to simulate the soil surface expected in the field. It was assumed that the soil was inert and would not emit significant amounts of CO_2.

The actual CO_2 flux from the box was determined using Equation A.1 and compared to the flux collected in the chambers at 0.000236, 0.000472, 0.000944, 0.001416, and 0.001888 m^3/s (0.5, 1, 2, 3, and 4 cfm) using Equation A.2. Flow rates of 0.000236 and 0.000472 m^3/s (0.5 and 1 cfm) produced erratic results (>80% error), probably due to the low air exchange rates per minute within the flux chambers. At 0.001888 m^3/s (4 cfm), the airflow rate diluted the samples to background concentrations, resulting in erroneous flux calculations. Flow rates of 0.000944 and 0.001416 m^3/s (2 and 3 cfm) worked well (25 to 40% error), depending on the magnitude of the flux exiting the box. Full testing with replications was performed for 0.000944 m^3/s (2 cfm) only (Figures A.3a and A.3b). A summary of the slope and intercept values for each replication and for each chamber can be found in Table A.1. The circular chamber had a tendency to underestimate the

actual flux while the rectangular chamber had a tendency to overestimate the actual flux, however, no distinct trends were observed.



(a) (b)

Figure A.3. Calibration of (a) rectangular flux chamber and (b) circular flux chamber at 2 cfm (3 reps). Chamber and actual fluxes have units of mg CO_2/m^2-s.

Table A.1. Summary of slope and intercept values for flux chamber calibration equations.

Chamber	Rep	Slope	Intercept	R^2
Rectangular	1	0.8095	-0.0475	0.97
Rectangular	2	1.858	-0.0642	0.94
Rectangular	3	1.1609	0.1125	0.97
Circular	1	0.6754	-0.118	0.98
Circular	2	1.1702	0.0116	0.96
Circular	3	0.6088	0.0395	0.90

The differences in the values for slope among the repetitions may be explained by the different operating conditions among each repetition. Since they were performed on different days, the changing atmospheric pressure and relative humidity may have skewed the results. The moisture content of the soil layer on top of the calibration box did not vary by more than 2% (w.b.) between each repetition. The changing ambient CO_2 concentration may also have affected the concentration gradient between the flux simulation box and the atmosphere. Nonetheless, these results indicate that, for the rectangular chamber design, the optimal sweep airflow rate was 0.944 L/s (2 cfm). Additionally, it was possible to establish a calibration equation for this chamber for each set of atmospheric conditions and ambient CO_2 concentration.

Another explanation for the varying value of slope was that the flux through the soil layer was 'short circuiting' and not emitting evenly across the entire surface area of the calibration box. The flux may have been higher outside the areas covered by the flux

chambers, resulting in a deflated flux chamber reading. Further testing where the top of the flux simulation box was closed except for the chambers was completed. Those results are not reported here.

Conclusions

The rectangular flux chamber allowed for calculation of emissions within 50% of the actual emissions when the flow rate of the sweep air was 0.944 L/s (2 cfm). This experiment also shows that calibration curves can be generated for these chambers, but calibration will be specific for each set of environmental conditions (temperature, humidity, etc.). Also, for proper calibration for odour emissions, an odour tracer should be used.

Appendix B—Odour Data

Table B.1. Summary of odour, hedonic tone and odour emission rate results from 2006 and 2007 data (including outliers). Different letters following mean values of Log OU and Hedonic Tone indicate significant differences within that group at the 95% level of confidence.

				Log OU			Hedonic Tone			Odour Emission Rate (OU/m^2-s)
	Group		n	Mean		SE	Mean		SE	Mean
2007	Species	dairy	24	2.68		0.083	2.86		0.110	1.40
		feedlot	24	2.44		0.034	2.94		0.130	0.80
		swine (s)	23	2.30		0.056	3.16		0.090	0.58
		poultry	24	2.64		0.052	2.80		0.075	1.28
		swine (l)	23	2.66		0.097	2.09		0.094	1.34
	Type	solid	71	2.46	a	0.063	2.97	a	0.059	0.84
		liquid	47	2.67	b	0.032	2.48	b	0.091	1.37
	Mode	surface	58	2.60	a	0.043	2.80	a	0.094	1.16
		injected	60	2.49	a	0.048	2.74	a	0.073	0.90
	Rate	0X	28	2.31	a	0.031	3.04	a	0.120	0.60
		1X	30	2.64	b	0.062	2.68	b	0.110	1.28
		2X	30	2.61	b	0.060	2.63	b	0.100	1.19
		3X	30	2.70	b	0.079	2.76	b	0.110	1.46
2006	Species	dairy	21	2.56	a	0.056	2.14	a	0.120	1.06
		swine	21	2.87	b	0.022	2.00	a	0.051	2.17
	Mode	surface	17	2.84	a	0.063	1.88	a	0.100	2.02
		injected	25	2.63	b	0.041	2.20	a	0.070	1.25
	Rate	0X	3	2.71	a	0.150	2.10	a	0.210	1.50
		0.25X	11	2.65	a	0.061	1.96	a	0.140	1.31
		0.5X	11	2.72	a	0.063	2.01	a	0.068	1.53
		1X	11	2.83	a	0.097	2.05	a	0.160	1.98
		2X	6	2.61	a	0.081	2.43	a	0.110	1.19

Note: A hedonic tone of 1 was labelled as "dislike extremely" and 9 was labelled as "like extremely". A hedonic tone of 5 was considered neutral.

Table B.2. Outliers (2006 and 2007 odour data). For all 2006 data, average value for Log OU = 2.71±0.25. For all 2007 data, average value for Log OU = 2.55±0.36. Data points beyond 3 standard deviations were considered outliers.

Year	Type	Species	Mode	Rate	Rep	Log OU
2006	Liquid	Dairy	Surface	1X	2	3.46
2007	Liquid	Swine	Injected	3X	1	3.91
2007	Liquid	Swine	Injected	3X	2	3.86

Table B.3. Summary of odour, hedonic tone and odour emission rate results from 2006 and 2007 data (excluding outliers). Different letters following mean values of Log OU and Hedonic Tone indicate significant differences within that group at the 95% level of confidence.

				Log OU			Hedonic Tone			Odour Emission Rate (OU/m^2-s)
	Group		n	Mean		SE	Mean		SE	Mean
2007	Species	dairy	24	2.68		0.083	2.86		0.110	1.40
		feedlot	24	2.44		0.034	2.94		0.130	0.80
		swine (s)	23	2.30		0.056	3.16		0.090	0.58
		poultry	24	2.64		0.052	2.80		0.075	1.28
		swine (l)	21	2.55		0.059	2.09		0.094	1.04
	Type	solid	71	2.46	a	0.063	2.97	a	0.059	0.84
		liquid	45	2.62	b	0.053	2.48	b	0.091	1.22
	Mode	surface	58	2.60	a	0.043	2.80	a	0.094	1.16
		injected	58	2.44	b	0.036	2.74	a	0.073	0.80
	Rate	0X	28	2.31	a	0.031	3.04	a	0.120	0.60
		1X	30	2.54	b	0.062	2.68	b	0.110	1.01
		2X	30	2.61	b	0.060	2.63	b	0.100	1.19
		3X	28	2.62	b	0.056	2.76	b	0.110	1.22
2006	Species	dairy	20	2.51	a	0.034	2.14	a	0.120	0.95
		swine	21	2.87	b	0.022	2.00	a	0.051	2.17
	Mode	surface	16	2.80	a	0.052	1.88	a	0.100	1.84
		injected	25	2.63	b	0.041	2.20	a	0.070	1.25
	Rate	0X	3	2.71	a	0.150	2.10	a	0.210	1.50
		0.25X	11	2.65	a	0.061	1.96	a	0.140	1.31
		0.5X	11	2.72	a	0.063	2.01	a	0.068	1.53
		1X	10	2.77	a	0.082	2.05	a	0.160	1.72
		2X	6	2.61	a	0.081	2.43	a	0.110	1.19

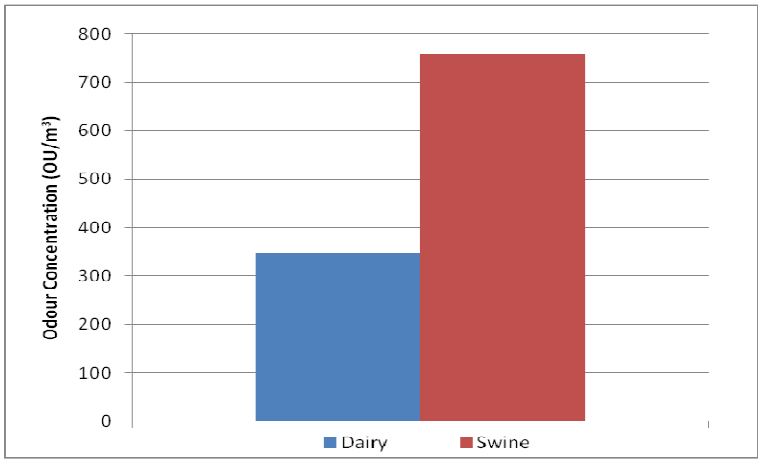
*Odour emissions from bare soil averaged 0.603 ± 0.0043 OU/m^2-s, suggesting that odours from solid swine manure are not statistically different than odours from bare soil.

Note: A hedonic tone of 1 was labelled as "dislike extremely" and 9 was labelled as "like extremely". A hedonic tone of 5 was considered neutral.

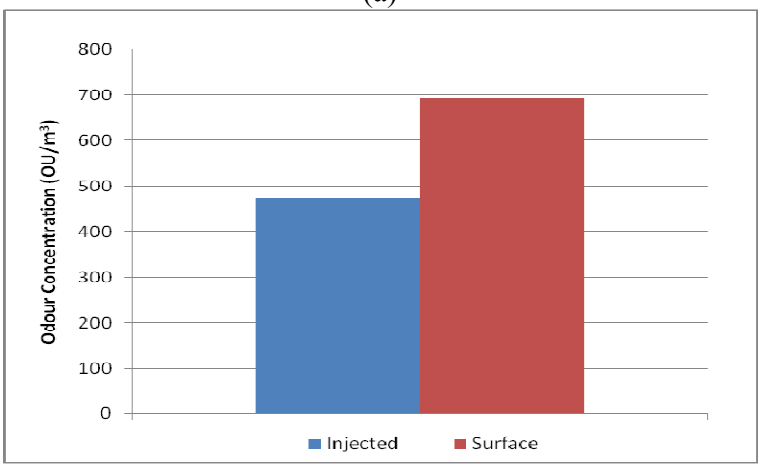
Table B.4. Summary of odour concentration (OU/m^3) and Log OU data.

Year	Type	Species	Mode	Rate	n	Concentration	Stdev	Log OU	Stdev	
2006	Liquid	Dairy	Injected	0.25X	3	288.7	95.3	2.4419	0.1614	
				0.5X	3	345	101.8	2.5255	0.1262	
				0X	1	263	*	2.5587	*	
				1X	3	263	71	2.4078	0.13	
				2X	3	288.3	92.4	2.4462	0.1302	
2006	Liquid	Dairy	Surface	0.25X	3	349	22.5	2.5422	0.0286	
				0.5X	2	362	0	2.5587	0	Note: 1 sample lost
				0X	1	362	*	2.5587	*	
				1X	1	912	*	2.96	*	Note: 1 outlier, 1 sample lost
2006	Liquid	Swine	Injected	0.25X	3	659.3	58.8	2.818	0.0383	
				0.5X	3	554	36.4	2.7429	0.0291	
				1X	3	816.3	94	2.9099	0.0501	
				2X	3	598.3	40.4	2.7763	0.0288	
2006	Liquid	Swine	Surface	0.25X	2	744	238	2.86	0.142	Note: 1 sample lost
				0.5X	3	991	136.8	2.9934	0.0579	
				0X	1	1024	*	3.0103	*	
				1X	3	849.3	108.5	2.9266	0.0579	
2007	Liquid	Dairy	Injected	0X	3	182.9	31.5	2.2579	0.075	
				1X	3	433	373	2.534	0.355	
				2X	3	316.7	108.1	2.4835	0.1505	
				3X	3	591	279	2.734	0.23	
2007	Liquid	Dairy	Surface	0X	3	138.5	45.7	2.124	0.1542	
				1X	3	1528	574	3.161	0.181	
				2X	3	1276	357	3.0939	0.1263	
				3X	3	1117	191	3.0437	0.0766	
2007	Liquid	Swine	Injected	0X	3	221.8	37.9	2.3416	0.0766	
				1X	3	461.3	48.3	2.6624	0.0452	
				2X	3	1026	887	2.91	0.351	
				3X	1	1290	*	3.1106	*	Note: 2 outliers
2007	Liquid	Swine	Surface	0X	2	209	92.4	2.298	0.199	Note: 1 sample lost
				1X	3	292.5	67.1	2.4584	0.1003	
				2X	3	271.1	61.3	2.4252	0.1043	
				3X	3	292.5	67.1	2.4584	0.1003	
2007	Solid	Feedlot	Injected	0X	3	250.7	20.5	2.3982	0.0348	
				1X	3	240.4	33.1	2.3783	0.06	
				2X	3	289.7	44.1	2.4584	0.0695	
				3X	3	240.5	33.3	2.3784	0.06	
2007	Solid	Feedlot	Surface	0X	3	232.1	53.3	2.358	0.1003	
				1X	3	219.82	14.26	2.3414	0.0287	
				2X	3	292.5	67.1	2.4584	0.1003	
				3X	3	651	370	2.743	0.334	
2007	Solid	Swine	Injected	0X	3	124.8	21.2	2.0918	0.076	
				1X	3	114.12	0.315	2.0574	0.0012	
				2X	3	126.8	35.6	2.0911	0.1267	
				3X	3	134.02	17.14	2.1247	0.0579	
2007	Solid	Swine	Surface	0X	2	198.1	57.6	2.2875	0.1281	Note: 1 sample lost
				1X	3	299.3	157.1	2.439	0.217	
				2X	3	490.9	155.1	2.6741	0.1537	
				3X	3	439.1	66.8	2.639	0.0695	
2007	Solid	Poultry	Injected	0X	3	378.4	48.4	2.5754	0.0579	
				1X	3	322.51	0	2.5085	0	
				2X	3	471.1	152.2	2.6591	0.1327	
				3X	3	367.1	113.8	2.5487	0.1498	
2007	Solid	Poultry	Surface	0X	3	261.1	92.4	2.399	0.1512	
				1X	3	1057	1076	2.88	0.418	
				2X	3	978	1055	2.823	0.452	
				3X	3	565	185	2.7345	0.1564	

2006 avg	568.8	84.3	2.708	0.075
2007 avg	459.8	181.8	2.529	0.140
max	1528	1076	3.161	0.452
min	114.12	0	2.0574	0



(a)



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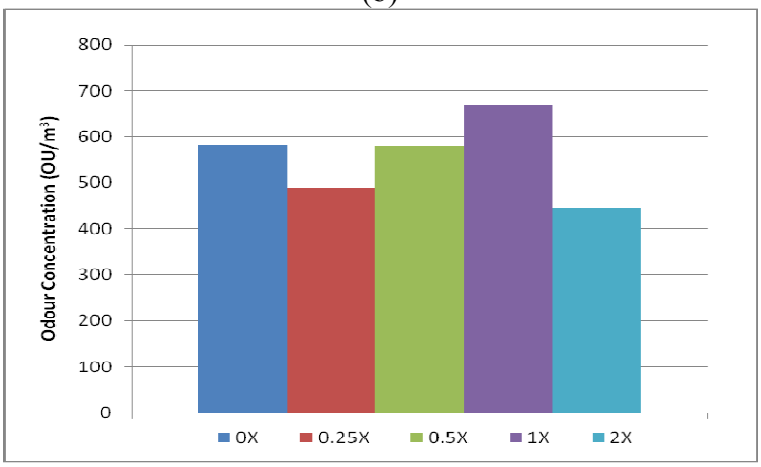


(c)

Figure B.1. Overall odour concentration (OU/m^3) data from 2006 a) effect of manure type, b) effect of application method, and c) effect of application rate.

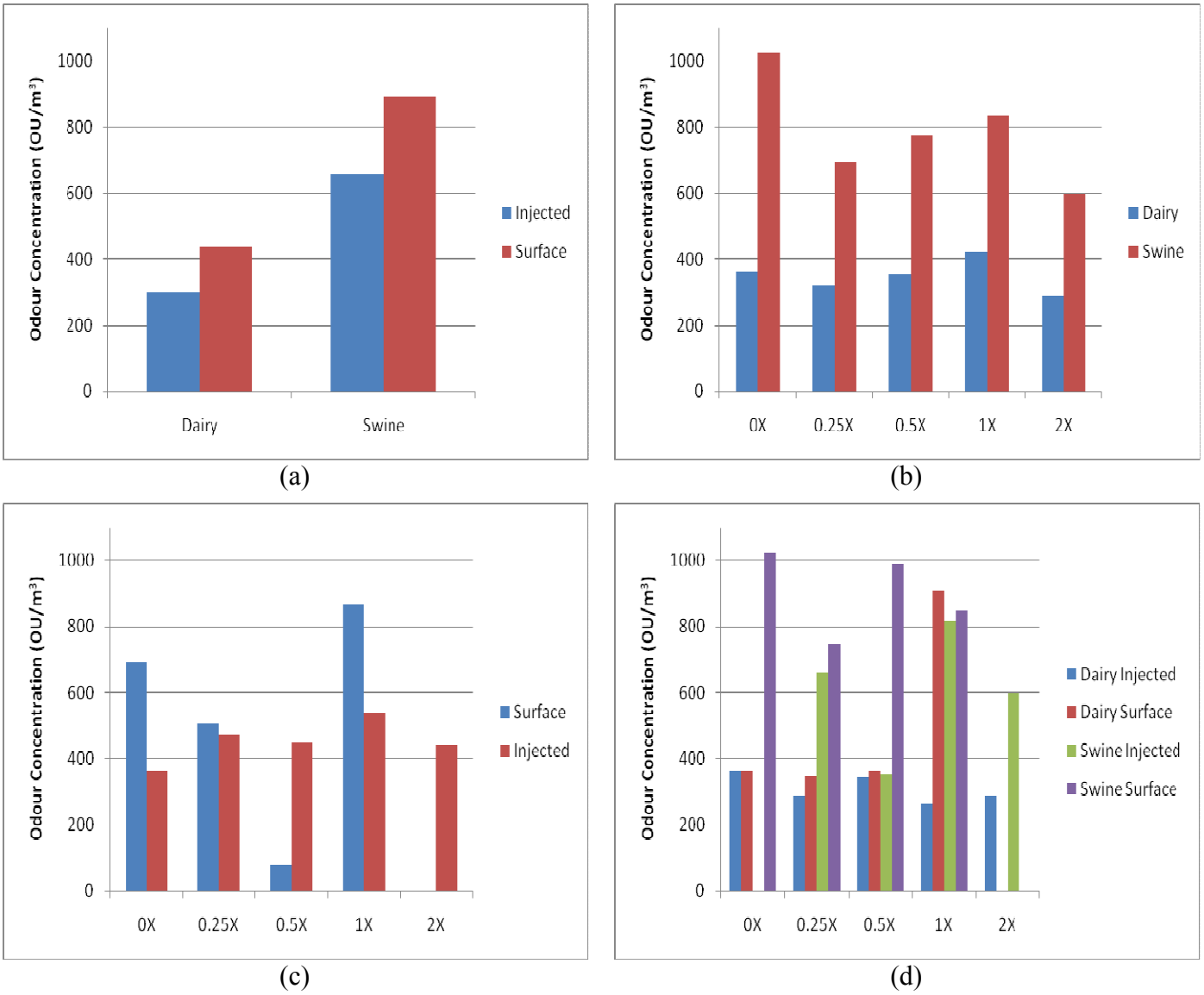


Figure B.2. Detailed odour concentration (OU/m^3) data from 2006 a) effect of application mode and manure type, b) effect of application rate and manure type, c) effect of application mode and application rate, and d) effect of manure type, application mode and application rate.

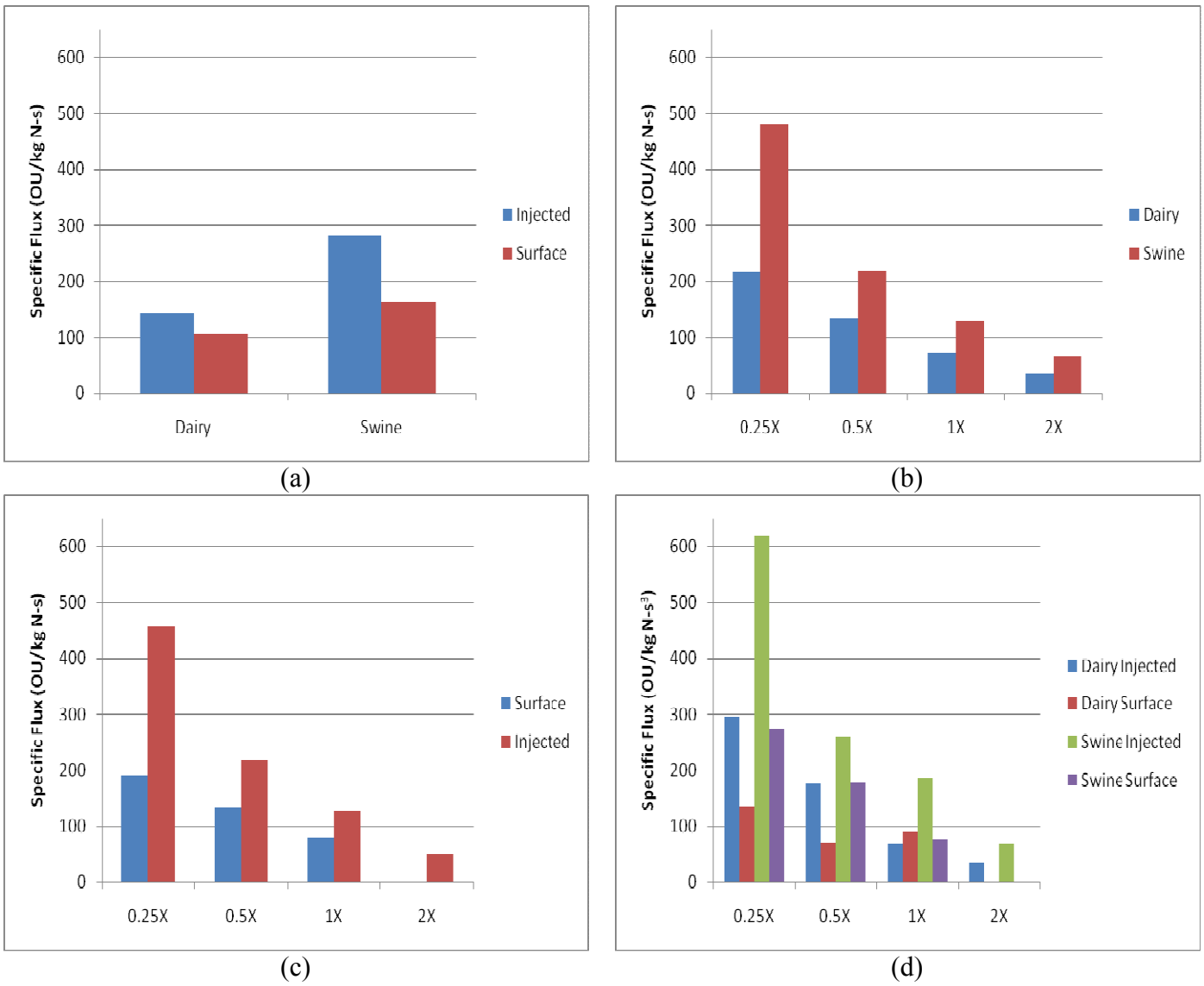


Figure B.3. Specific odour rate (OU/kg N-s) data from 2006 a) effect of application mode and manure type, b) effect of application rate and manure type, c) effect of application mode and application rate, and d) effect of manure type, application mode and application rate.

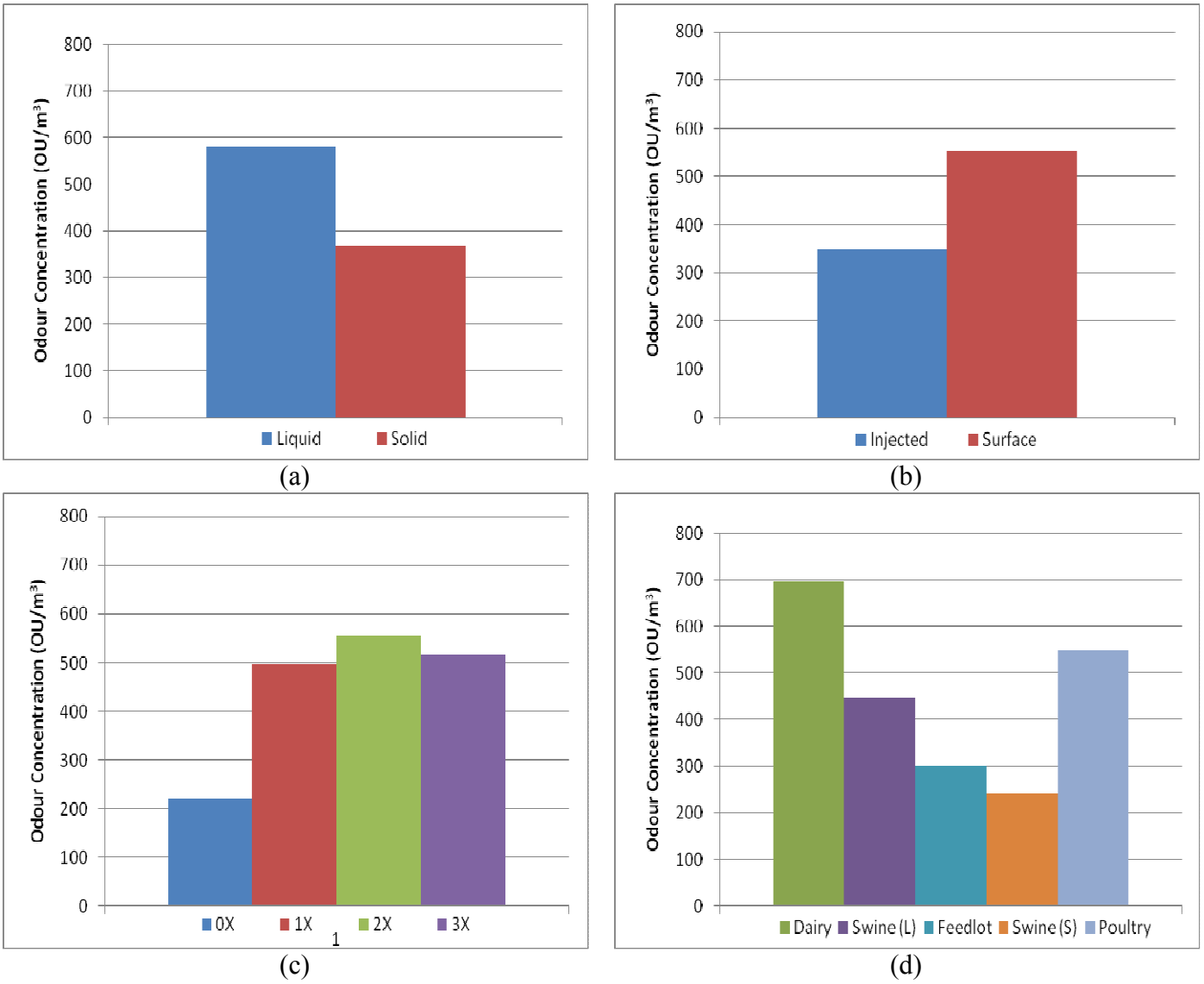


Figure B.4. Overall odour concentration (OU/m^3) data from 2007 a) effect of manure type, b) effect of application method, c) effect of application rate, and d) effect of manure species.

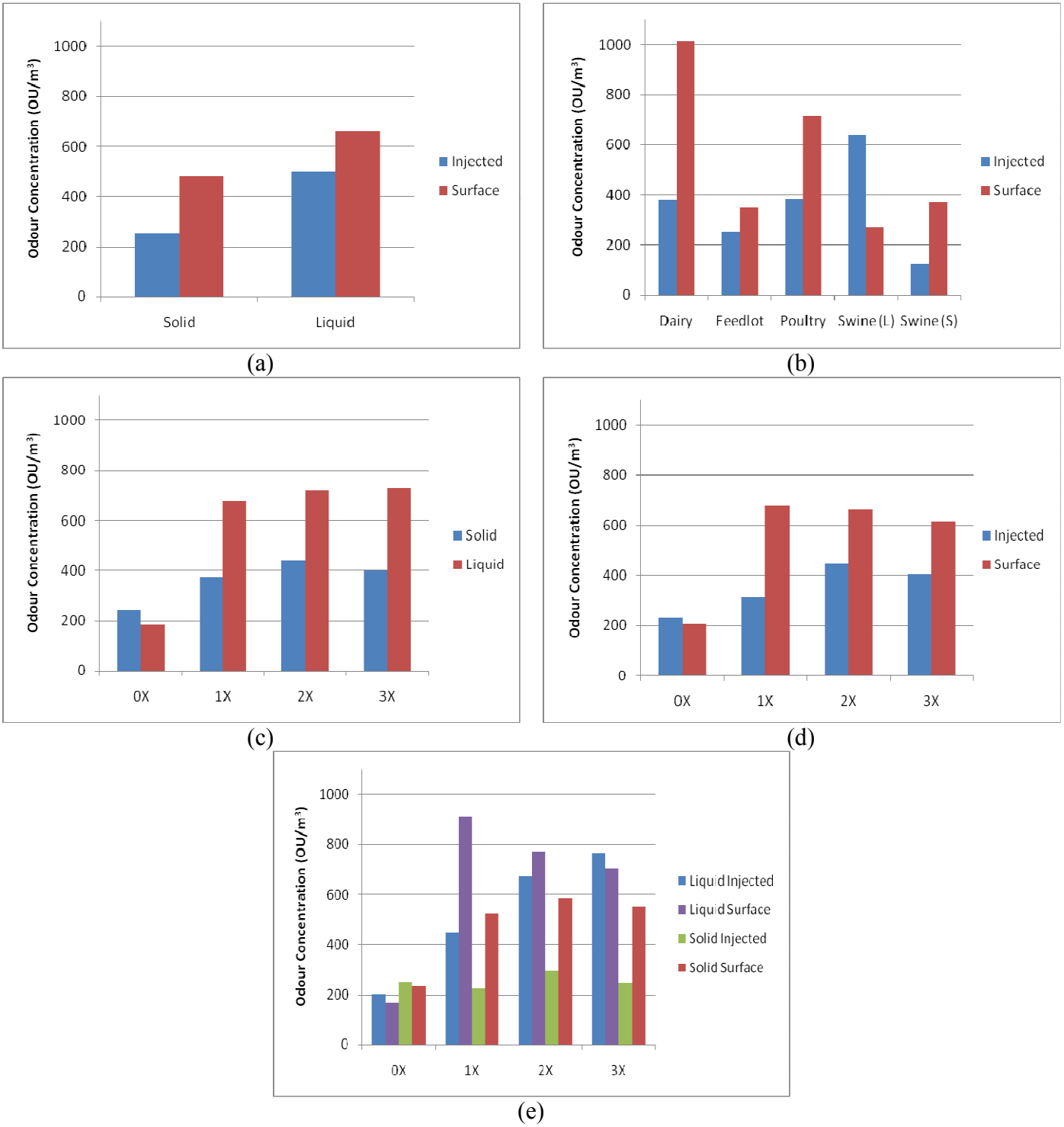


Figure B.5. Detailed odour concentration (OU/m^3) data from 2007 a) effect of application mode and manure type, b) effect of application mode and manure species, c) effect of manure type and application rate, d) effect of application mode and application rate, and e) effect of manure type, application mode and application rate.

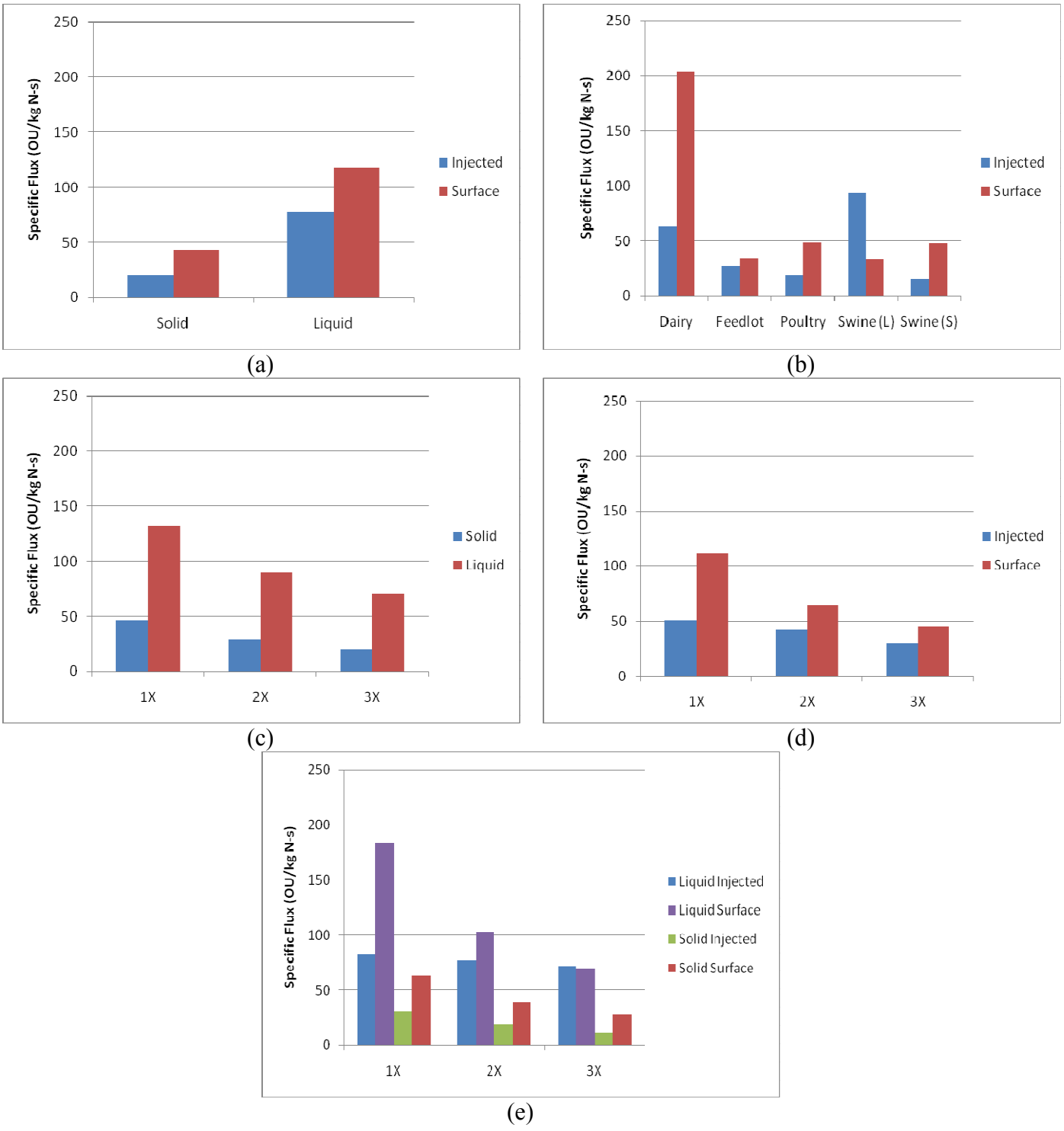


Figure B.6. Specific odour rate (OU/kg N-s) data from 2007 a) effect of application mode and manure type, b) effect of application mode and manure species, c) effect of manure type and application rate, d) effect of application mode and application rate, and e) effect of manure type, application mode and application rate.

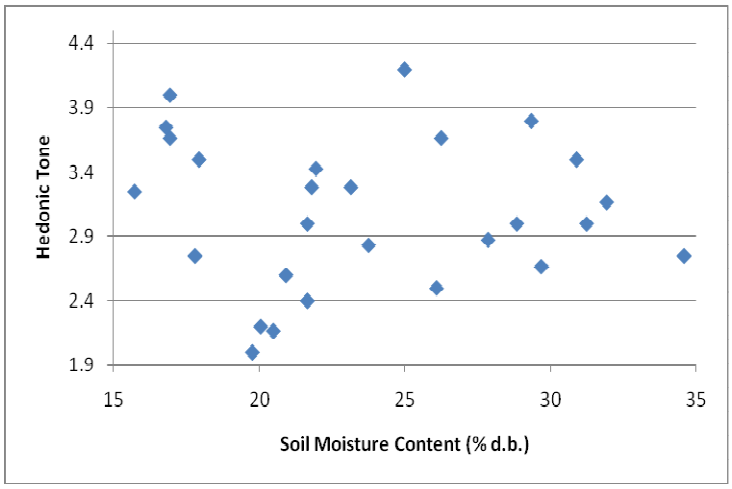


Figure B.7. Effect of soil moisture content (% d.b.) on hedonic tone from control (0X) plots.

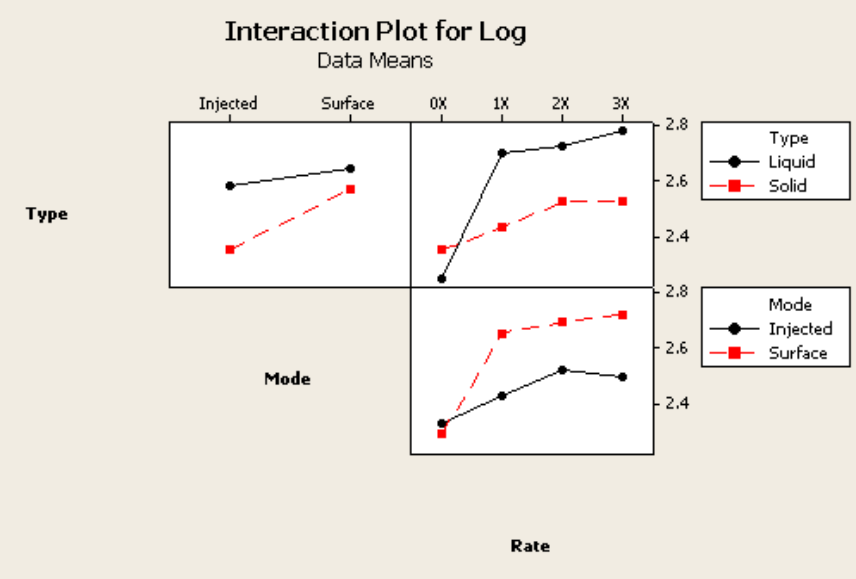


Figure B.8. Effect of treatment interactions on log OU data. Only the type*rate interaction was statistically significant (P=0.031).

Appendix C—Uncertainty Analysis for Odour Flux Calculation

The equation used to calculate odour emission rate from a flux box was

$$E = C * \frac{Q}{A} \quad \text{(C.1)}$$

Where E = odour emission (OU/m^2-s),
C = odour concentration of sample (OU/m^3),
Q = flow rate in chamber (m^3/s), and
A = soil area enclosed by chamber (m^2).

Therefore, the uncertainty in odour emission depends on the uncertainty in:

1. odour concentration measurement
2. flow rate measurement
3. area measurement

1. The uncertainty in odour concentration measurement is high because of the huge number of factors that affect odour production, collection and measurement. From the entire 2006 and 2007 data set, the standard deviation of the odour concentration measurements of like treatments (maximum 3 reps) ranged from 0 to 1075 OU/m^3. The average value of the standard deviations was 133 OU/m^3. The odour concentration measurements ranged from 114 to 1528 OU/m^3 with an average value of 514 OU/m^3. An overall uncertainty of 26% (133 divided by 514) for odour concentration measurement is low, but this value was based on this data set which was relatively large. [C = 514 ±133 OU/m^3]
2. The uncertainty in the flow rate measurement was based on the precision and accuracy of the rotameter used to measure the flow rate, which was set to 0.0009439 m^3/s. The specifications for the rotameter stated an uncertainty of 10%. [Q = 0.0009439±0.00009439 m^3/s]
3. The uncertainty in the area of the chamber is related to the uncertainty in the measurement of the length and width. The uncertainty in the measurement of the length and width comes from the tolerance of the measuring tape used (1 cm). If the length was 0.8 m (±0.01 m) and the width was 0.4 m (±0.01 m), the maximum area is 0.3321 m^2 and the average area is 0.32 m^2. Therefore the uncertainty in the area measurement is ±0.0121 m^2. [A = 0.32±0.0121 m^2]

To complete the uncertainty analysis, Equation C.1 was partially differentiated with respect to each of the 3 variables outlined above.

$$\frac{\partial E}{\partial C} = \frac{Q}{A} \quad \text{(C.2)} \qquad \frac{\partial E}{\partial Q} = \frac{C}{A} \quad \text{(C.3)} \qquad \frac{\partial E}{\partial A} = \frac{-CQ}{A^2} \quad \text{(C.4)}$$

The partial derivatives (C.2, C.3 and C.4) were assessed using average values for concentration, flow rate and area (C = 514 OU/m^3, A = 0.32 m^2, Q = 0.0009438 m^3/s). The overall error in the E calculation was then calculated using Equation C.5.

$$\% \text{ error in E} = \frac{\sqrt{\left(\frac{\partial E}{\partial C}\partial C\right)^2 + \left(\frac{\partial E}{\partial Q}\partial Q\right)^2 + \left(\frac{\partial E}{\partial A}\partial A\right)^2}}{E} \quad \text{(C.5)}$$

The ∂C, ∂Q and ∂A values were 133 OU/m^3, 0.00009439 m^3/s and 0.0121 m^2 respectively. The E value in the denominator was calculated using Equation C.1. and typical C, A and Q values. This resulted in a percent error in odour flux calculation of 28%. It was clear from the analysis that the error in odour concentration measurement and the error associated with the flow rate measurement contributed the most to this uncertainty. Improving the accuracy of odour concentration measurement by 10% (so overall uncertainty in odour concentration measurement is only 15%) would reduce the uncertainty in the flux calculation to 18%.

Appendix D—Summary of Literature Values

Table D.1. Summary of literature values for odours from manure spreading.

Reference	Collection Method	Odour Values and Units (as reported)	Treatments	Comments
Pain et al. (1988)	Wind tunnel (1 m^2, 1 m/s)	285 OU <70 OU 34 to 11 OU/m^2-hr	2 hrs after spreading 24 hrs after spreading Separated cattle and pig slurry	
Pain et al. (1990)	Wind tunnel (1 m^2, 1 m/s)	34 – 1100 OU/m^3 4.5 – 49.7 x 10^3 OU/L	Raw vs digested pig slurry application	No difference between two diets
Misselbrook et al. (1997)	Wind tunnel (1 m^2, 1 m/s)	102 – 879 OU/m^3	Cattle slurry application up to 15 hrs after application	Odours returned to background within 2 hrs
Moseley et al. (1988)	Wind tunnel (1 m^2, 1 m/s)	50 – 250 OU/m^3	Raw vs digested pig slurry by different methods	Surface = slipper foot >>injection = control for pig slurry
Hanna et al. (2000)	Wind tunnel (0.787 m^2, 2.2 m/s)	12 – 240 OU 140 – 1604 OU 25 – 136 OU	Untreated Broadcast at application Sweep at application	Odours returned to background within 24 hrs
Pahl et al. (2001)	Wind tunnel (0.5 m^2, 0.35 m/s)	448 OU/m^3 420 OU/m^3	Injection Surface	No reps, no control
Rahman et al. (2004)	Wind tunnel (0.3 m^2, 0.3 m/s)	377 OU/m^3 732 OU/m^3	50 mm injection depth 100 mm injection depth	No correlation between application rate and odour
Chen et al. (2001)	Static chamber (1 m^2)	234 – 1094 OU/m^3		Surface = aerated surface > slipper foot = injection
Hansen et al. (2006)	Static chamber (3.12 m^2, 1.87 m^3)	150 – 1000 OU/m^3		Untreated slurry > digested slurry > digested + separated slurry
Lindvall et al. (1974)	Chamber/tunnel (unknown specs)	1.50 log OU 4.09 log OU	Injected Surface	Aerobic treatment of slurry and solid cattle manure reduced odours, as did ammonium persulphate additive
Lau et al. (2003)	Flux chamber (0.0645 m^3, 0.19 m^2, 10 L/min)	39000 OU, 28647 OU/L, 34.21 OU m/s 3215 OU, 2440 OU/L, 2,82 OU m/s	Splash plate immediately following application Sub-surface deposition 2.5 hrs after application	
Pain et al. (1991)	TPS (micromet)	183 – 1076 OU/m^3 <100 OU/m^3 Max 350x10^3 OU/s-m^3 slurry	Immediately after application 24 hrs after application Pig and cattle slurry for a variety of application methods	
Mkhabela et al. (2007)	TPS (micromet)	1-203 OU/m^3 0.8 – 2.8x10^6 OU/m^2	Application rates, rainfall, slurry dilution, time after application	
Smith et al. (2007)	TPS (micromet)	34 – 108 OU/m^3 2.2 – 11.0 OU/m^2-s 0.55 – 1.3x10^6 OU/m^2	Manure type, application rates, rainfall, time after application	
Phillips et al. (1990)	Micromet	28 OU/L 35 OU/L 133 OU/L 182 OU/L 249 OU/L 6520 OU/L 200,000 – 50,000 OU/m^2-hr	Background Hoses Shallow injection Deep injection Splash plate Irrigation gun Immediately to 24 hrs after application	
This study	Flux chamber (0.944 m^3/s, 0.323 m^2)	552 OU/m^3 (1.16 OU/m^2-s) 348 OU/m^3 (0.90 OU/m^2-s)	Surface application Subsurface application	Includes a variety of manure species (solid and liquid) and three application rates

Chapter 4

4.0 Greenhouse Gas Emissions from Land Application of Manure

Greenhouse gas (GHG) emissions from agricultural activities such as land application of livestock manure cannot be ignored when assessing overall emissions from anthropogenic sources. The magnitude of these emissions will be influenced by management practices such as manure placement during land application. The objective of this work was to compare GHG fluxes resulting from the surface and subsurface application of liquid and solid manure. For this comparison, all measurements were made 24 hours after application. The results showed that subsurface application significantly increased carbon dioxide equivalent (CO_2-e) fluxes for both solid and liquid manure. The overall CO_2-e fluxes from the injected treatments were 3.2 times higher than CO_2-e fluxes from the surface applied plots, mainly due to a pronounced increase in N_2O fluxes which was likely caused by increased denitrification rates. The CO_2-e fluxes from the liquid manure applications were also higher than the CO_2-e fluxes from the solid manure applications, probably due to higher levels of ammonium available for nitrification and subsequent denitrification. The CH_4 fluxes were generally low and were not influenced by the treatments in this study. For this particular study, the specific fluxes (total flux per kg N applied) were not influenced by application rate, indicating that GHG emissions from manure applications were approximately proportional to the amount of manure applied.

4.1 Introduction

During the last 150 to 200 years, human activity has increased the atmosphere's content of carbon dioxide (CO_2) by 30%, of methane (CH_4) by 145%, and of nitrous oxide (N_2O) by 15% based on International Panel on Climate Change (IPCC) data (Greatorex, 2000). In addition, with the near elimination of chlorofluorocarbons (CFC's), N_2O is now the principal anthropogenic ozone-depleting substance (Ravishankara et al., 2009). These greenhouse gases (GHG) also contribute to the "greenhouse effect" of the atmosphere which is believed to play a major role in the global warming of Earth's climate (IPCC, 2007). The Kyoto Protocol, a multi-national agreement, was put in place at the end of the twentieth century with the goal of significantly reducing anthropogenic emissions of these greenhouse gases. Canada's commitment under the Kyoto Protocol was to reduce net annual greenhouse gas emissions by 6% relative to the 1990 levels of 608 Mt by 2008-2012 (Kebreab et al., 2006). This commitment has resulted in widespread research on emission reducing strategies and technologies that cover all aspects of society including manufacturing, transportation, industry, and agriculture. More recently, the Conference of Parties (COP) meeting of the IPCC held in Copenhagen, Denmark in 2009 has further emphasized the urgent need to limit anthropogenic GHG emissions, including those from agricultural sources.

It has been estimated that agricultural activities contribute to 20% of anthropogenic GHG emissions (Lovanh et al., 2008) and more specifically to 60 to 80% of total N_2O emissions (Jarecki et al., 2008). Agricultural emissions include CO_2 from burning fossil fuels, CH_4 from enteric fermentation in ruminant animals, CO_2 and CH_4 from storage of livestock manure and N_2O from fertilizer and manure application to land. The land application of manure and fertilizers contributes to 50% of Canadian agricultural GHG emissions (Kebreab et al., 2006) and is the main source of agricultural N_2O because fertilizer and manure applications significantly increase microbial production of N_2O from soils (Davidson, 2009). Nitrous oxide's high global warming potential (298 times that of CO_2, over 100 years (IPCC 2007)) makes it a large contributor to GHG budgets.

Soil surface N_2O emissions following application of animal manure are estimated to account for approximately 3.5 billion tonnes of carbon dioxide equivalents (CO_2-e) annually in Canada (Desjardins and Riznek, 2000) or 9% of all anthropogenic sources of N_2O (Rochette et al., 2004). Moreover, the addition of manure to soil results in complex biological and chemical interactions among the soil, water and air (Ginting et al., 2003). This suggests that emissions from manure application are transient, difficult to predict and depend on several uncontrollable factors. Nevertheless, because N_2O production is sensitive to environmental conditions and management practices, there exists a high potential for mitigating emissions resulting from land application of manure.

Despite the Kyoto Protocol and the need to mitigate GHG emissions, there is even greater public pressure and emphasis on reducing nuisance odour emissions associated with manure spreading. Strategies to that effect may include diet manipulation, manure additives, timing of application with wind and/or rainfall, and burying or injecting the manure into the ground. Sub-surface application of both solid and liquid manure is the most common method to reduce odours from manure spreading, but it also has the potential to increase N_2O production due to increased anaerobic microbial activity beneath the soil surface (Wulf et al., 2002b). Although reducing odour emissions is important in the short term to help sustain the livestock industry, the long term effects of increased GHG emissions may hinder the industry in the future. The International Panel on Climate Change (IPCC) has recognized that studies are required on the interactions between these gases because it is of concern that strategies to reduce emission of one gas may increase emission of others (IPCC, 1997).

Over 65% of the land applied with manure in Canada in 2005 received solid manure (Statistics Canada, 2006) and the most common practice to reduce odour emissions is sub-surface application (See Table 2.1 in Chapter 2). While the effectiveness of subsurface application of solid manure on reducing odour emissions was assessed in Chapter 3, the impact of subsurface application of manure on GHG emissions needs to be investigated. The impact of manure type and application rate on relative GHG emissions

from manure spreading also needs to be studied so that the carbon footprint of different manure management strategies can be better assessed.

4.2 Literature Review

4.2.1 GHG Emission Measurement from Area Sources

Agricultural GHG emissions have been collected and measured in a variety of ways. Non-point source emissions from a large area (such as a field that has been treated with manure) are most commonly monitored by means of static or non-steady state chambers (Chadwick et al., 2000; Ginting et al., 2003; Lessard et al., 1996, 1997; Lovanh et al., 2008; Petersen, 1999; Rochette et al., 2000a, 2000b; Van Groenigen et al., 2004; Wulf et al., 2002b; etc.) or micrometeorological techniques (Sharpe and Harper, 1997; Sherlock et al., 2002; Wagner-Riddle et al., 1997). A limited number of studies have reported on the use of dynamic (steady state) chambers for GHG emission measurement (Christensen et al., 1996; Chadwick et al., 2000). Steady state chambers are typically not useful for measuring relatively low GHG fluxes, as is the case from manure applications. This is due to the low sensitivity of analytical equipment such as gas chromatography. Refer to Chapter 3 for details on steady-state or dynamic chambers.

4.2.1.1 Static Chambers

Static (or non-steady state) chambers allow gases emitted from a surface to collect within a known volume during a known period of time. If the chamber also includes a vent to the atmosphere for pressure equilibration, it can also be referred to as a vented flux chamber. Sub-samples are drawn from the chamber at known intervals so the rate of change in gas concentration can be determined, typically using regression analysis. The rate of change in gas concentration is used with chamber volume and surface area and gas density to calculate surface gas flux using Equation 4.1.

$$F = \rho \frac{V}{A} \frac{\Delta C}{\Delta t} \quad (4.1)$$

where: F = surface gas flux (mg/m^2-s),

ρ = density of gas (kg/m^3),

V = volume of chamber (m^3),

A = area of chamber (m^2), and

ΔC/Δt = rate of change of gas concentration (ppm/s).

Other forms of this equation that account for the temperature and partial pressure of water vapour in the chamber have also been used (Rochette and Hutchinson, 2005 in: Rochette et al. 2008; Ginting et al., 2003; Hutchinson and Livingston, 1993) because temperature and pressure inside the chamber can affect the build-up of gases.

Since there is no sweep air flow through the chamber, the gases are not diluted, making the measurement of low fluxes possible and reasonably accurate. However, fluxes measured using chamber methods are often highly variable or erratic due to the spatial and temporal variability of non-point emission sources. Using numerous chambers and frequent sampling can help account for these variations, but this approach is time consuming and expensive. Another way to account for spatial variability of N_2O fluxes is to use "mega-chambers". Mega-chambers allow trace gas fluxes to be averaged over several tens of square meters and typically consist of tent-like, tunnel shaped constructions (Greatorex, 2000) which are also very cumbersome.

Another major drawback of static chambers is their effect on the microclimate of the measured surface. The build-up of gases in the chamber can theoretically suppress emissions from the soil over time by decreasing the concentration gradient between the soil surface and the atmosphere immediately above it. This will result in a non-linear gas concentration build-up in the headspace and underestimation of the flux when Equation 4.1 is used. Hutchinson and Mosier (1981) developed a formula to account for this. By assuming that there is a plane of constant gas concentration not affected by the chamber,

that the diffusion of the gas is steady-state, and that gas concentration increases linearly with depth, these authors have suggested that the gas flux can be calculated using Equation 4.2.

$$f_o = \frac{\rho V (C_1 - C_o)^2}{At(2C_1 - C_2 - C_o)} \ln \frac{C_1 - C_o}{C_2 - C_1}, if \frac{C_1 - C_o}{C_2 - C_1} > 1 \qquad (4.2)$$

where: f_o = gas flux (mass per unit area per unit time),

ρ = density of gas (mass per unit volume),

V = volume of chamber,

A = cross sectional area of chamber,

t = time interval,

C_o = concentration of sub-sample drawn at time = 0,

C_1 = concentration of sub-sample drawn at time = t_1, and

C_2 = concentration of sub-sample drawn at time = t_2 ($t_2 = 2t_1$ for the equation to be valid).

GHG fluxes from the same manure application experiment were calculated using both Equations 4.1 and 4.2 by Lovanh et al. (2008). These authors found that GHG fluxes calculated using linear regression and Equation 4.1 were consistently lower than fluxes calculated using Equation 4.2.

The size of the chamber should be such that it maximizes surface area (accounts for spatial variation) while minimizing the headspace volume (for accurate determination of low gas concentrations). Caution must be used with short chambers (<50 mm height) since a small error in volume determination caused by uneven soil surfaces will have a greater impact on flux calculation than with taller chambers (Rochette et al.,1997; Rochette and Bertrand, 2008). A chamber height of 150 mm is appropriate for most agricultural situations (Rochette and Bertrand, 2008). The geometry of the chamber (square, rectangular, or cylindrical) has little impact on its performance as long as adequate air mixing is achieved (Rochette and Bertrand, 2008). To ensure adequate

mixing of the headspace volume and to minimize the effects of gas build-up, forced air movement should be included inside the chamber. Rochette and Bertrand (2008) discuss the benefits of a variable speed fan to simulate ambient mixing.

The length of time a chamber is deployed and the sampling interval varies widely in literature, ranging from 20 minutes to several hours. Hutchinson and Mosier (1981) stated that shorter enclosure times (less than 30 minutes) are preferred for N_2O flux measurement because shorter times result in fewer disturbances of the microsite and results in smaller changes in the N_2O production rate. However, enclosure time should be such that the increase in gas concentration is large enough to be reliably measured by the instrumentation. In other words, the concentration increase measured over each time interval must be at least three times greater than the standard deviation of repetitive analyses of a standard gas mixture; otherwise, random analytical errors can have an inordinately large influence on the flux computed using Equation 4.2 (Hutchinson and Mosier, 1981).

Pressure disturbances due to wind and air movement around the chambers will also influence the gas flux from the soil (Hutchinson and Livingston, 1993). Positive and negative pressure variations are then generated around the chamber, and unsteady increases of the gas concentrations may be observed (Rochette et al, 1997). Fan-induced turbulence can also influence flux measurements. Adding a vent to the chamber permits pressure equilibration between a closed cover and its surroundings, reducing the effect of the cover on the microsite. Vent design should be such that it transmits barometric pressure fluctuations while minimizing air leakage or contamination (Hutchinson and Mosier, 1981). Vent dimensions for a 60 L static chamber are outlined in Rochette and Bertrand (2008).

Thermal insulation and reflective covering are recommended to minimize heating by solar radiation (Hutchinson and Mosier, 1981). Un-insulated chambers may lead to significant temperature changes of the headspace during deployment, altering the volume of gas sampled by up to 5% (Greatorex, 2000). In addition, temperature fluctuations can have an impact on trace gas production, consumption and transport processes in the

covered soil. However, the effects of temperature perturbations are minimal over relatively short deployment times (Hutchinson and Livingston, 1993).

Other changes to the soil system resulting from chamber deployment include compaction of the soil or changes to biological systems (when the collar is inserted into the soil, root systems or the soil can be disturbed), affecting the overall gas flux (Hutchinson and Livingston, 1993). Static chamber enclosures are also impractical for tall stands of crop or grass. Most chamber methods are not suitable for studying dynamic events like rainfall or diurnal temperature fluctuations, since the deployment may rapidly interfere with the soil conditions (Greatorex, 2000).

Rochette et al. (1992) discussed the operation of dynamic open and dynamic closed static chambers. Dynamic open chambers operate in the same way as dynamic chambers with a sweep air stream but, in dynamic closed systems, air is circulated from the chamber to a gas analyzer and returned to the chamber. Dynamic closed chambers can facilitate shorter deployment periods by providing a greater number and frequency of gas concentration measurements as well as provide early detection of experimental problems (Rochette and Bertrand, 2008). However, dynamic closed chambers are limited to gas species for which a suitable portable analyzer is available and the short deployment times make it difficult to measure low emission rates (i.e.; N_2O, CH_4) (Rochette and Bertrand, 2008).

4.2.1.2 Micrometeorological Methods

Micrometeorological techniques measure the turbulent transfer of gases from the ground surface to the lower atmosphere. They are able to measure gaseous fluxes over a larger area than is possible with static or dynamic chambers, with the added advantage that they do not disturb the conditions at the soil surface. The limitations of these techniques involve the requirement for expensive and sophisticated equipment, relatively level terrain and complex calculations (Bogner et al., 1997 in: Greatorex, 2000).

Among the micrometeorological techniques, the eddy covariance or eddy correlation technique is the most direct one for flux measurements. The vertical flux of the gas is

calculated as the mean product of the fluctuations of gas concentration and the vertical wind speed at a given height above the surface over a given period. It requires simultaneous, high frequency measurement of the vertical air velocity and the concentration of the target air constituent. Gas sensors are required to measure the target gas concentration with a time resolution of 10 Hz or better. For trace gas analysis, laser and infrared spectroscopy devices are used.

Gradient techniques, in contrast to eddy covariance, represent an indirect measurement of trace gas fluxes. In this method, the transport of a trace gas due to the turbulent air movement is described in analogy to the molecular diffusion. Gradient measurements require continuous and simultaneous measurement of trace gas concentration, temperature and the horizontal wind velocity at various heights above the ground. An advantage of the gradient technique over the eddy correlation technique is that it does not require instruments with a high measuring frequency. This can lead to savings in equipment and maintenance costs. However, the use of gradient techniques is limited to situations in which the air has blown over a homogeneous exchange surface for a long distance, up to 500-1000 m (Denmead and Raupach, 1993).

Tracer methods rely on the simultaneous measurement of the concentrations of both the target gas and an inert tracer released at a known rate (Greatorex, 2000). If the tracer gas is released in a way that resembles the emission of the target gas, the concentration ratio of the two gases measured downwind can then be related to the ratio of their fluxes. Tracer methods can be a valuable alternative to micrometeorological methods when sources are limited in size and the micrometeorological conditions are unfavourable. However, small errors in estimation of the tracer gas release rate can lead to sizeable errors in the estimation of the target gas emission rate. Also, tracer ratio methods are restricted to situations where the plume of interest is not mixed with another nearby source. Also, the target gas concentration must be sufficiently high to distinguish it from background levels (Greatorex, 2000).

The mass balance micrometeorological technique is useful for small plot research because it does not require the large fetches needed for gradient and eddy correlation approaches (Denmead and Raupach, 1993). Plot dimensions are typically tens of meters instead of hundreds of meters and the instrumentation requirements can be quite simple. This method equates the flux of gas into the atmosphere from a treated area of limited upwind extent with the rate at which it is transported by the wind across the downwind edge (Denmead and Raupach, 1993). However, the upwind concentration profile must be measured as well as the downwind and the calculation of flux requires subtraction of experimentally determined data, which can be an error-prone procedure (Denmead and Raupach, 1993). Therefore, this technique is best suited to experimental treatments where the fluxes are large compared to normal emissions. The main advantage of the mass balance technique is that, in certain situations, it is possible to infer the surface flux from measurements of the horizontal flux at just one height above the plot center (Denmead and Raupach, 1993).

Measurements of the concentration of the gases for all micrometeorological methods can be made using a variety of techniques (gas chromatography, Fourier transform infrared spectroscopy, or tuneable diode laser spectrometers). The type of instrumentation used will depend on the expected magnitude of the concentration. Nitrous oxide fluxes from agricultural soils are often large enough to result in measurable concentrations, but methane fluxes are often harder to detect because of their low concentrations. Micrometeorological methods are usually applied for nitrous oxide flux measurements, simply because methane emissions from agricultural soils are of very marginal importance in the greenhouse gas balance (Greatorex, 2000).

Micrometeorological techniques do not interfere with the emission source, can handle measurements in crop canopies and allow the user to study dynamic events. They also account for spatial variability and are suitable for inventory studies rather than process-oriented studies. However, the experimental site needs to be flat and homogeneous for the entire fetch in all wind directions. The difference in mean trace gas concentrations determined between the ground level and higher levels is typically very small and may

lead to substantial analytical error. In addition, even when the fetch requirements (up to 500-1000 m) are met, it is unrealistic to expect micrometeorological methods to provide reliable flux measurements 24 hours a day (Denmead and Raupach, 1993). Methods of measuring the low wind speeds that occur at night are imprecise, rain and dew can cause hazards, boundary layers are often not well developed at night, and rapid changes in the stratification of the boundary layer can make time-averaged concentration profiles unreliable (Denmead and Raupach, 1993). Another drawback of direct micrometeorological techniques such as eddy correlation is the interference of vegetation (Chahuneau et al., 1989 in: Rochette et al. 1992).

In some cases, combinations of two or more methods are employed to measure gas fluxes from agricultural soils when more than one gas is of interest. For example, Sherlock et al. (2002) utilized different methods for different gases. Since ammonia is very reactive with water compared with CH_4 and N_2O, the elevated ammonia concentration in a static chamber will reduce ammonia emissions from the soil covered by the chamber. The ammonia emissions, therefore, were measured with a micrometeorological mass balance technique that does not affect the ammonia concentration above the soil. Static chambers were used to measure surface fluxes of both CH_4 and N_2O since these gases were less reactive with water and were much less affected by increases in chamber headspace concentration.

4.2.1.3 Comparison of Collection Methods

The performance of dynamic open and dynamic closed systems was compared by Cropper et al. (1985 in: Rochette et al., 1992). Dynamic open chambers yielded larger soil respiration estimates than static chambers. Rochette et al. (1992) saw the same trend and noted that the difference in measured fluxes between dynamic closed and static chambers was larger at higher CO_2 fluxes. Marshall and Debell (1980) drew the same conclusion for ammonia capture following urea fertilization. The static chambers resulted in the lowest amounts of volatile ammonia while the dynamic closed chambers resulted in the highest amount of capture (Marshall and Debell, 1980), presumably due to the suppression of emissions due to the lower concentration gradient in the static chamber.

Rochette et al. (1997) stated that there was a good correlation between static chambers and dynamic closed chambers for individual soil textures, indicating that there could be an interaction between soil properties and the microclimate within the chamber.

A short study by Rochette et al. (1997) (41 hrs during one weekend) showed a positive correlation between carbon dioxide flux measured by a dynamic closed chamber and eddy correlation. Christensen et al. (1996) monitored N_2O emissions using micrometeorological and dynamic chamber techniques (3 sizes of chamber and a sweep flow rate of 1.5 L/min). The authors concluded that there was no bias between the different approaches used to measure the N_2O emission and that the precision of the measurements was determined by the spatial variability of the N_2O emissions at the site and the variability inherent in the individual techniques (Christensen et al., 1996).

4.2.2 GHG Emissions from Fertilizer and Manure Application in Literature

There have been numerous laboratory, plot and field scale studies comparing GHG emissions from manure application to GHG emissions resulting from fertilizer applications. Lab scale studies allowed greater control over variables such as soil properties and weather conditions. Researchers conducting lab scale studies typically used packed soil cores, incubation chambers, and headspace covers to study the effects of various treatments on gas production rates. These methods allowed assessment of denitrification and nitrification rates using nitrification inhibitors to determine the origin of N_2O emissions. Plot and field scale studies allowed for a more realistic investigation of the effects of manure type (liquid vs. solid) and application method (surface with and without incorporation, trail hose application, aeration, injection, etc.), as well as application rate, soil texture, and other variables on GHG emissions. Those studies and their main findings are summarized here.

4.2.2.1 Emissions from Fertilizer vs. Manure Application

Several studies have found that denitrification rates were higher after manure application than after fertilizer application at similar N application rates (Paul and Zebarth, 1997; Barton and Schipper, 2001; etc.). Most authors agreed that, unlike fertilizer application, manure not only affects soil N, but is also a source of available C compounds which can stimulate denitrification and affect the denitrifier community abundance and activity (Miller et al., 2009; Rochette et al., 2000b). Increased C availability can enhance denitrification by providing C to denitrifiers and by increasing soil respiration, resulting in decreased oxygen concentrations (Beauchamp et al., 1989 in: Miler et al., 2009). Because of this dependence on available C, Miller et al. (2009) suggested that emission mitigation strategies should focus on C availability as well as N management. Alternatively, it was postulated that manure may also decrease N_2O fluxes in the short term because manure organic N may be less readily available for nitrification and denitrification processes (Rochette et al., 2008). Therefore, the net impact of manure application on N_2O in a given situation will depend on manure characteristics, soil physical properties, soil C and N levels and climatic conditions (Rochette et al., 2008).

Several field studies found that GHG emissions from manure application were higher than emissions from fertilizer applications with comparable N application rates (Akiyama and Tsuruta, 2003; Barton and Schipper, 2001; Meng et al., 2005; Wagner Riddle et al., 1997, Lemke et al., 1999; Helgason et al., 2005; Ellert and Janzen, 2008). Additionally, Lessard et al. (1997) found no significant differences among CH_4 fluxes from application of stockpiled solid manure, composted solid manure, and fertilizer, but trends showed that manured plots had higher fluxes. Similarly, Petersen (1999) found no significant difference in N_2O emissions between manure and fertilizer application, but the highest N_2O flux came from the slurry applied treatment.

Conversely, Rochette et al. (2000a) reported that manure application had little or variable effect on CO_2 emissions from 2 rates of pig slurry and 1 rate of commercial fertilizer application. Also, Bouwman et al. (2002) published a summary of field studies that showed that the N_2O emitted per kg of N added was 20% lower for animal manures than

for synthetic N fertilizers. This could have been due to the volatilization of ammonia in some types of manure reducing the actual N applied as well as the fact that manures are often applied to perennial grasses which have a high N uptake potential, reducing N available for N_2O (Rochette et al., 2008).

Finally, Van Groenigen et al. (2004) measured N_2O fluxes from 4 rates of commercial fertilizer and cattle slurry applications, and combinations of the two sources on two different soils. The authors hypothesized that the combination treatment would result in higher fluxes because of the abundance of readily available C and N, but this was not the case. For both sandy and clay soils, fertilizer application resulted in the highest N losses, followed by slurry application and finally combination applications (Van Groenigen et al., 2004). Perala et al. (2006) also showed that slurry application produced higher cumulative N_2O emissions compared to slurry+fertilizer and fertilizer alone, but there were no significant differences. On the other hand, Dittert et al. (2005) did observe a significantly higher N_2O-N flux from a slurry+fertilizer application compared to when the fertilizer and slurry were applied alone due to the availability of both N and C.

4.2.2.2 Comparison of Emissions from Different Manure Types

Several studies have noted that GHG emissions from liquid manure applications differ from emissions from solid manure applications. In a laboratory scale study, it was found that applications of liquid manure resulted in immediate and intense denitrification while those of solid manure resulted in less intense but prolonged denitrification (Loro et al., 1997). Tenuta et al. (2000) also reported that solid manure applied to the soil provided a "more sustained release" of available C as the bedding material decomposed, promoting denitrification enzyme activity for longer periods. The majority of solid manure C and N is in the form of organic matter, but anaerobic conditions during storage of liquid manure results in high levels of easily decomposable C species and mineral N, resulting in higher emissions from liquid manure applications in the short term (Rochette et al., 2008). Differences in emissions between solid and liquid manure applications can be explained by the easier access to the highly diluted substrates in slurry than in solid manure, which usually forms clods which physically protects inner substrates from decomposers

(Rochette et al., 2000a). Solid manure application adds recalcitrant forms of C and N to the soil, suggesting that although their potential to stimulate nitrification and denitrification may be less than that of liquid manures, the stimulatory effect of solid manures may extend over longer periods (Lemke et al., 2009).

Rochette et al. (2008) referred to several studies that stated that N_2O losses were higher from soils amended with liquid than solid manures (Loro et al., 1997; Chadwick et al., 2000), although they found no significant trend in their study. In a compilation of information, Gregorich et al. (2005) concluded that annual N_2O fluxes from solid manure applications were lower than N_2O fluxes from liquid manure applications. The authors noted that the N in solid manure would become available over a longer period, but the lower emissions following application of solid manure may have resulted from the uptake of available N by growing plants. Gregorich et al. (2005) also noted that short measurement periods (i.e.: one year) following application of solid manure may not fully account for all of the manure-induced emission of N_2O due to long-term mineralization of C and N. Indeed, Mogge et al. (1999 in: Rochette et al., 2008) reported that emission from soils with a long history (30 yr) of repeated application of solid manure were higher than emissions from liquid manured soils and concluded that nitrification was the major contributor to N_2O production.

GHG emissions also vary with animal type due to different diets, feed conversions, and management of the manure (Chadwick et al., 2000). Chadwick et al. (2000) monitored N_2O emissions from pig slurry, beef manure, dairy slurry, layer manure and pig manure. The pig slurry and beef manure resulted in immediate emissions of N_2O, likely due to rapid nitrification of NH_4 or denitrification of NO_3 already in manure (beef manure) and the high C content and moisture content (pig slurry) (Chadwick et al., 2000). N_2O from other manure types were not significantly different from untreated control plots (Chadwick et al., 2000). Watanabe et al. (1997) noted that CO_2 and N_2O-N fluxes were higher from swine excrement applications than from cattle excrement applications, but N contents were not normalized. In a lab scale study, Chadwick and Pain (1997) noted that pig slurry generated more CH_4 than dairy slurry in clay soils, but there was no difference

between manure types on sandy soils. This may have been due to the lower C:N ratio of the pig slurry and the rapid infiltration and oxidation in the sandy soil (Chadwick and Pain, 1997).

Manure treatments such as anaerobic digestion, slurry separation, slurry aeration, and straw covered manure storages may also affect GHG emissions after land application. For example, anaerobic digestion alters the availability of C in the substrate, affecting the potential N_2O production (Petersen, 1999). Amon et al. (2005) monitored CH_4 and N_2O emissions after application of dairy cattle slurry with several treatments (control, slurry separation, anaerobic digestion, slurry aeration and straw covered storage). The proportion of CH_4 emissions from land application ("total" emissions are from storage and spreading) were highest for the separated slurry while the untreated slurry produced no CH_4 emissions after application (Amon et al., 2005). The proportion of N_2O emissions from land application was highest for separated slurry followed by straw covered, untreated, aerated, and digested slurry (Amon et al., 2005).

4.2.2.3 Comparison of Emissions from Different Application Methods

The greater contact of injected slurry with soil can induce favourable conditions for N_2O and CH_4 formation because of restricted aeration in the vicinity of the injected manure (Wulf et al., 2002b; Flessa and Beese, 2000). Many researchers have hypothesized that injection or subsurface application of manure will promote denitrification (Comfort et al., 1988; Wulf et al. 2002b). However, Wulf et al. (2002b) noted that literature results on the effect of injection and incorporation on GHG after manure application are contradictory as some show an increase in emissions due to injection and others show no differences. For example, in a laboratory scale study, Dendooven et al. (1998) found no difference in CO_2 and N_2O production within 15 days of injecting pig slurry versus surface application. Flessa and Beese (2000), however, did note significantly higher N_2O and CH_4 emissions from an injection treatment compared to a surface treatment, but CO_2 flux was not affected by application method. Lovanh et al. (2008) and Sistani et al. (2008) showed that surface application of swine slurry produced higher, but not significantly

higher, fluxes of N_2O compared to row injection and aerway injection (surface application over artificially perforated or aerated soil). The aerated treatment resulted in the highest CH_4 flux (Sistani et al., 2008). Weslien et al. (1998) reported slightly, but not significantly, higher emissions after banding+harrowing compared with trenching, shallow injection and band-spreading. Harrowing was thought to spread around the manure under the soil, creating more hot spots and partially anaerobic regions while injection resulted in complete denitrification, producing N_2 instead of N_2O (Weslien et al., 1998). However, Perala et al. (2006) showed that slurry injection produced higher cumulative N_2O emissions than slurry incorporation, but the difference was not significant. The authors also noted that CH_4 oxidation (uptake) was highest for the injected treatments, but fluxes were all close to zero (Perala et al., 2006).

Wulf et al. (2002b) compared GHG emissions from splash plate, trail hose, trail shoe and injection methods. Results indicated that trail hose application with immediate incorporation resulted in the lowest GHG emissions on arable land while trail shoe application had the smallest risk of high GHG emissions on grassland. Wulf et al. (2002b) stated that, in terms of CO_2 equivalents, the increase in N_2O emissions after injection might be as high as the reduction of NH_3 losses or, as in the case of injection on grassland, might even increase overall GHG emissions. Injection also resulted in prolonged CH_4 emissions (although they still lasted less than 4 days) (Wulf et al., 2002b). The flux patterns for different application techniques varied, but cumulative emissions showed injection increased overall emissions (Wulf et al., 2002b). The authors attributed this result to the promotion of anaerobic sites and diffusion constraints that occur with the injection technique.

4.2.2.4 Correlating GHG Emissions with Soil Properties

Microbial activity and GHG emissions are highly dependent on soil properties such as nutrient content, moisture and oxygen availability. For example, Bergstrom et al. (2001) attributed the N_2O production after fertilizer application to the nitrification of ammonium as regulated by soil water and NO_3 contents. However, Barton and Schipper (2001) concluded that there was no good correlation between N_2O production and soil properties

due to variability in threshold values existing for nitrification and denitrification and the lack of ability to measure soil properties in soil microsites.

Soil texture (fine vs. coarse) has often been found to play a role in GHG emissions after N application. The small pores and lower oxygen content in fine textured soils likely promote denitrification and N_2O emission (Gregorich et al., 2005; Bouwman et al., 2002; Van Groenigen et al., 2004), but Jarecki et al., (2008) and Mkhabela et al. (2006 in: Jarecki et al., 2008) observed higher N_2O emissions from coarse textured soils than from fine textured soils. Rochette et al. (2008) also noted that, for certain periods of measurement, N_2O fluxes from clay soil were lower than from sandy soil, presumably due to slow gas diffusion in wet clay that allowed further reduction of N_2O into N_2 before it reached the soil surface. Less reduction occurred in the sandy soil, resulting in higher N_2O fluxes (Rochette et al., 2008). However, both field and modeling studies have concluded that N_2O emissions from agricultural soils were on average higher from fine than from coarse textured soils (Rochette et al., 2008). Overall emissions of CO_2 and CH_4 were higher from a clay soil than a sandy soil in a lab scale study as well (Chadwick and Pain, 1997). This is supported by the lower redox potentials of fine-textured soils as a result of lower air filled porosity and greater resistance to O_2 diffusion (Rochette et al, 2008). Lower total emissions from sandy soil may also be due to nitrate leaching and rapid crop uptake (Van Groenigen et al., 2004).

Level of soil compaction played a role in N losses from soils applied with fertilizer and cattle slurry in Hansen et al. (1993). There was no difference in N_2O fluxes between fertilizer and slurry applications for uncompacted soil, but a significantly higher N_2O flux came from the compacted, fertilized treatment (Hansen et al., 1993).

Water filled pore space (WFPS) influences oxygen availability and diffusivity and is also thought to impact GHG emissions. Results from a study by Bateman and Baggs (2005) indicated that the majority of N_2O emissions from a fertilized silt loam soil with a water filled pore space (WFPS) between 35 and 50% were the result of the nitrification process. In that study, N_2O emissions increased by a factor of 10 at a WFPS of 60% and N_2O

emissions were entirely due to the denitrification process at a WFPS of 70%. Davidson (1991 in: Jarecki et al., 2008) provided a general relationship between WFPS and N_2O emissions between 30 and 90% with a peak N_2O production occurring at approximately 65% WFPS. Jarecki et al. (2008) noted that within a given soil type, fertility regime, and cropping system a relationship like this may be valid, but generalizations across soils and management systems are likely to be poor. In fact, Maljanen et al. (2007 in: Jarecki et al., 2008) noted that peak N_2O emissions continued to increase with WFPS in the range of 80 to 90%. Conversely, Sharpe and Harper (1997) used irrigated swine effluent and micrometeorological techniques and found that N_2O fluxes were not related to soil water content. Petersen (1999) also found that soil water content had no effect on N_2O emissions from fertilizer and slurry application.

Manure type and application method are also thought to influence soil WFPS by adding moisture and changing the soil structure, thus influencing GHG emissions. Perala et al. (2006) noted that slurry injection increased WFPS to levels that promote denitrification and Sherlock et al. (2002) stated that slurry addition made soil anaerobic for a "lengthy period". Comfort et al. (1988) reported that the water content in the injection zone remained higher than the surrounding soil for 99 days after application. However, Rochette et al. (2004) concluded that pig slurry application had no effect on soil water content and temperature.

Miller et al. (2009) monitored microbial (denitrifier) populations and N_2O emissions after liquid dairy and swine manure applications on a lab scale and found no relationship between denitrifier abundance and denitrification and N_2O emissions. Comfort et al. (1990) used a lab scale experiment with nitrification inhibitors to compare nitrification and denitrification after injection of dairy slurry. Simulated rainfall had little effect on denitrification and N_2O production, possibly due to a limitation in readily oxidizable carbon (C) (Comfort et al., 1990).

Other soil properties like temperature, NO_3 content and pH are also believed to influence GHG emissions. Meng et al. (2005) reviewed several studies that reported that lower soil

temperatures significantly reduced the nitrification rates but did not greatly decrease denitrification. Another reference in Meng et al. (2005) stated that there are threshold values for WFPS, temperature and NO_3 concentration, under which N_2O fluxes are relatively low. Petersen (1999) reported that the soil NO_3 content had no effect on N_2O while Goodroad et al. (1984) concluded that soil pH did not affect N_2O fluxes.

4.2.2.5 Effect of Application Timing on GHG Emissions

Proper timing of manure application is important to minimize nutrient losses. Applying the nutrients when the plants require them (i.e.: active growing season) is thought to reduce the chances of leaching, runoff, and volatilization losses. Lower N_2O fluxes from spring applications were reported in Thompson and Pain, (1989), Allen et al. (1996), and Chadwick (1997) as reported in Rochette et al. (2004). However, Rochette et al. (2004) and Barton and Schipper (2001) reported higher emissions following spring applications than fall applications due to higher soil temperature and moisture levels in the spring. Rochette et al. (2004) also hypothesized that wet and cool fall conditions limited net nitrification and resulted in little accumulation of NO_3, thus limiting potential for subsequent denitrification and N_2O emissions. However, other N losses occur during fall and winter (runoff, leaching) that are not accounted for in either study, so overall N losses between the spring and fall treatments may have been similar with the spring losses being mainly gaseous. Wagner Riddle et al. (1997), Grant et al. (2004), Smith et al. (2004) and Wagner Riddle and Thurtell (1998) reported on the significance of spring thaw emissions of N_2O. Reasons for high fluxes during spring thaw involve the rapid nitrification-denitrification at the soil surface and/or the release of N_2O accumulated below the frozen layer in the soil profile (Cates and Keeney, 1987 in: Wagner Riddle et al. (1997)). These authors stressed that spring thaw N_2O fluxes should not be neglected when considering livestock GHG contributions.

4.2.2.6 Effect of Application Rate on GHG Emissions

Nitrous oxide fluxes increased linearly with fertilizer application rate in the information compiled by Gregorich et al. (2005). Generally, for manure application, GHG emissions

in the short term increase with application rate for both solid (Chang et al., 1998) and liquid (Paul et al., 1993) manure since any N not used by the plants is available for denitrification. However, other studies that measured cumulative N losses over longer periods found that rate of manure application had little effect on overall N_2O emissions (Hansen et al., 1993). Lessard et al. (1996) noted that application rate did not affect GHG flux but did affect NH_4-N and NO_3-N contents in soil profile. In Rochette et al. (2000b), the addition of the second 60 Mg/ha resulted in a greater incremental increase of emissions than the first 60 Mg/ha, suggesting a non-linear relationship between application rate and N_2O flux. Van Groenigen et al. (2004) also concluded that N_2O emissions were not linearly related to N application rates and the effect of application rate varied with type and application rate of fertilizer.

In terms of C fluxes from different rates of manure application, Rochette et al. (2000a) reported a linear response of C oxidation to the amount of liquid manure added, suggesting that there were no physical or chemical limitations to increased microbial activity with increased amount of liquid manure added. In contrast, Gregorich et al. (1998) reported that the CO_2 flux increased proportionately less for the second increment of manure added than for the first increment.

4.2.2.7 Diurnal Variations, Time to Peak and Duration of GHG Emissions

The overall flux of gases depends on many soil environmental factors including soil moisture and temperature so the daily variation and length of time between application and peak fluxes can vary widely. Several researchers have noted diurnal variation in N_2O fluxes. However, Akiyama and Tsuruta (2003) observed no clear pattern for daily peak fluxes, indicating that there is no time of day where maximum or minimum fluxes can be consistently measured (Goodroad et al., 1984).

Large fluxes of N_2O can occur weeks or even months following manure application due to a large rainfall event. In other cases, the largest flux of N_2O can occur shortly after application (within 24 hrs) as in Barton and Schipper (2001), Sharpe and Harper (1997)

and Dittert et al. (2005). Paul et al. (1993) noted that N_2O fluxes peaked within 4 days of application. Lessard et al. (1996) reported that 67% of total N_2O emitted occurred in the first 7 weeks following application. Rochette et al. stated that the effect of manure application on N_2O flux was limited to 30 days (2000b) or 60 days (2008) following application. Watanabe et al. (1997) reported that N_2O fluxes decreased to background levels (emissions from bare soil) within 110 days of manure application. They noted varying times to peak flux between winter and autumn experiments, presumably due to soil temperature differences (Watanabe et al., 1997). Other studies have shown highly variable time courses for peak response following animal waste application (Sharpe and Harper, 2002; Cabrera et al., 1994; etc.)

Methane emissions following manure spreading are typically short-lived because the majority of CH_4 flux from manure amended soils comes from the volatilization of CH_4 compounds in the manure. In Chadwick et al. (2000) and Chadwick and Pain (1997), emissions of CH_4 began immediately and more than 90% of CH_4 emitted was lost in the first 24 hrs in most cases. Sherlock et al., (2002) and Dittert et al. (2005) also noted that CH_4 emissions commenced immediately after application and peaked within 12 hrs of application. Weslien et al. (1998) also noted that the highest emissions of methane took place immediately after spreading using a variety of methods and were hardly detectable during the following measurements for most of the treatments.

Carbon dioxide fluxes are also sensitive to environmental factors, but the majority of CO_2 emissions following manure spreading occurred within 70 days of application (Rochette et al., 2000a). Ginting et al. (2003) noted that soil receiving manure or compost had similar CO_2 emission as the control or fertilized soil as early as one month after application.

4.2.2.8 Reported Fluxes

Tables E.1 to E.3 in Appendix E contain a complete listing of literature values for reported GHG flux values, including the measurement technique, gases measured, units of measurement and treatment applications in tabular form.

4.2.3 Modeling GHG Emissions from Fertilizer and Manure Applications

Manure handling and application methods affect not only the magnitude of the initial flux of GHG after application, but also the emission rate trend over time after application. For example, Loro et al. (1997) noted in their lab-scale study that emissions from solid manure applications lasted longer than emissions from liquid manure applications, likely due to the high levels of C in solid manure mineralizing over time and becoming available to the denitrifiers. In addition, the increased contact with microbes due to injection of manure may promote N_2O emissions in the short term, but rapid decomposition beneath the soil surface may mean that fluxes a few days after application are reduced. Some studies that reported on the effect of application technique on GHG fluxes only measured fluxes one or two times after application (Lovanh et al., 2008, Sistani et al., 2008) while others continually monitored fluxes over the course of 2 to 18 weeks (Weslien et al., 1998, Perala et al., 2006, Flessa and Beese, 2000, Wulf et al., 2002b). Of the studies that measured cumulative losses over a longer period, only Wulf et al. (2002b) found that injection resulted in significantly higher GHG emissions on a field scale. Collecting continuous GHG flux data from sites over several weeks is labour-intensive and does not always provide further insight or ability to clearly distinguish treatment effects. Therefore, a model that simulates the environmental conditions and nutrient transformations after manure application may be a more efficient approach to the prediction of the effect of management practices on total GHG emissions.

The mass balance of soil gas must take account of three mechanisms: 1) microbiological production, 2) diffusive transport, and 3) input to or output from soil N_2O reservoirs (Yoh et al., 1997). The mechanisms responsible for and interacting with gaseous movement in soils include adsorption, diffusion, volatilization, degradation, leaching, mineralization, and immobilization turnover. Several well established models exist for N transformation prediction, including the DeNitrification-DeComposition model (DNDC, Li and Aber, 2000) and the *ecosys* model (Grant et al., 2006). The DNDC model is a computer simulation model of carbon and nitrogen biogeochemistry in agro-ecosystems. DNDC

can be used for predicting crop growth, soil temperature and moisture regimes, soil carbon dynamics, nitrogen leaching, and emissions of trace gases including N_2O, CH_4, and CO_2 (DNDC, 2009). In the *ecosys* model, the key biological processes (mineralization, immobilization, nitrification, denitrification, root and mycorrhzial uptake) controlling the generation of N_2O are coupled with the key physical processes (convection, diffusion, volatilization, dissolution) controlling the transport of the gaseous reactants and products of these biological processes. These models have been used on a regional scale to predict GHG losses from agro-ecosystems and can be used to help predict the impact of different manure management strategies on overall GHG emissions. The application of these and other models to estimate emissions from manure spreading is discussed in Chapter 6.

4.2.4 Identification of Research Gaps and Objectives

Research on emissions from land application of manure usually focuses on one type of gas. For example, ammonia emissions from manure spreading have been reported by, among others, Bittman et al., (2005), Huijsmans et al., (2001), Wulf et al. (2002a), and Rodhe et al., (2004); and odour emissions are discussed by Hanna et al., (2000), Lau et al., (2003), Pain et al., (1991), and Smith et al., (2007). The emissions of GHG's have been investigated by Amon et al., (2005), Chadwick et al., (2000), Lessard et al., (1996, 1997), and Rochette et al., (2000a, 2000b, 2004, 2008). Very few researchers have evaluated both GHG and odour emissions from the same land application experiment. The International Panel on Climate Change (IPCC) has recognized that studies are required on the interactions among gases because it is of concern that strategies to reduce emission of one gas may increase emission of other ones (IPCC, 1998).

Furthermore, the majority of research to date on GHG emissions resulting from the land application of manure has focused on liquid manure, even though more than two thirds of land applied with manure in Canada receives solid or composted manure (Statistics Canada, 2006). Thus, there exists a distinct need for research on emissions from solid manure application. Another important element to consider is the impact of manure

management systems, such as surface broadcasting or injection of manure, on GHG emissions. The injection or incorporation of manure into the soil has the potential to increase these GHG emissions from manure spreading, which is an important consideration when attempting to assess agriculture's contribution to a region's total GHG emissions. With new plans and strategies being put in place to reduce global GHG emissions, it is important to carefully analyze emissions that result from new technologies or practices. There are very few comprehensive studies that have addressed the effect of subsurface application on GHG emissions, particularly for solid manure.

Finally, since manure type and application method are likely to affect microbial activity and emissions for up to a year after application, the emission rate over time relationship must be examined. This will provide a more accurate assessment of the impact of manure management practices on the overall emissions.

Therefore, the objective of this research was to compare GHG emissions between liquid and solid manure and surface and subsurface application. Specific objectives included:

- to evaluate existing equipment and protocols for GHG emission determination following land application of manures and, if required, develop new protocols and equipment for sample collection,
- to evaluate the relative GHG emissions from various types of solid and liquid manure with both surface and sub-surface application, and
- to examine and modify an existing nutrient transformation model to better predict GHG emissions following surface and sub-surface land application of liquid and solid manure (refer to Chapter 6).

4.3 Materials and Methods

4.3.1 Selection of Sampling and Measurement Techniques

Since this study involved comparisons among multiple treatments, the static (closed) chamber technique was selected to collect GHG flux data. Gas concentrations were assessed using gas chromatography. Refer to Appendix F for gas chromatography specifications.

The significance and magnitude of the rate of increase of gas concentration in the chamber headspace to determine gas flux was evaluated on a case by case basis. In many cases, the Hutchinson and Mosier flux model (Equation 4.2) was technically valid. However, linear and polynomial regression allowed more reliable calculation of the rate of change of concentration and offered the ability to perform a statistical test to determine the significance of the regression model. Since the chamber enclosure time was short in this study, the effect of the chamber on the concentration gradient was thought to be minimal, eliminating the need for the Hutchinson and Mosier flux model. Therefore, fluxes were calculated using Equation 4.1 and linear or quadratic regression was used to determine the rate of change in gas concentration. Sample calculations and a comparison of flux values calculated using Equations 4.1 and 4.2 can be found in Appendix G.

4.3.1.1 Description and Operation of Static Chamber

Two identical static chambers were constructed for assessing the GHG emissions from surfaces applied with manure and are depicted in Figure 4.1. The chambers were 0.60 m in diameter (0.283 m^2 surface area) and 0.15 m high, made of corrugated PVC tube. The chambers were capped with 6.35 mm thick PVC plates. Small, battery powered (9 volt) computer cooling fans were wired inside the chamber to facilitate good mixing of the sample gases. The cap also included a sampling port and septum and an open port (30 mm high, 10 mm diameter) for pressure equalization and depth measurements. The exterior of the chambers were painted white to minimize adsorptive heating inside the

chamber during deployment. The internal headspace varied, depending on how deeply the chamber was inserted in the soil, but the average headspace was 0.040 m^3.

(a) (b)

Figure 4.1. Static chambers for greenhouse gas emission measurement a) exterior view and b) interior view.

Samples were collected for GHG flux determination approximately 24 hrs after application of manure. Initial testing showed that, for samples collected immediately after application, the rate of concentration change in the headspace was too erratic to calculate reliable flux estimates. Although CH_4 fluxes after manure application are generally short-lived (less than 12 hrs), N_2O and CO_2 were considered the main gases of concern, so sampling was delayed until 24 hrs after application. All GHG samples were collected in the morning between 0900 and 1200 to minimize the effects of diurnal variations.

For each gas measurement, the chamber fan was turned on and the chamber was deployed on the ground at the sampling site. The chamber was quickly pushed into the soil approximately 5 cm to form a good seal and prevent the gases from escaping the chamber. Pushing the chamber into the soil is thought to affect long-term emissions by altering the soil and root structure, but it will have a minimal impact on short-term emissions. To collect a sample from the chamber, a needle was inserted into the septum, the 20 mL syringe was purged 3 times with the headspace air without withdrawing the needle, and the 20 mL sample was drawn. The sample was then injected into a 12 mL evacuated Exetainer™ containing a dessicant to absorb any moisture in the sample. Samples were drawn from the sampling port at equal intervals (5, 10, 15 minutes) after

chamber deployment. Upwind ambient samples were collected periodically during the sampling session to represent the time = 0 sample. Ambient samples were drawn into the syringe from a height of 1 m above the ground.

The 15-min enclosure time was selected due to the logistical constraints of coordinating the field testing with odour measurements. The results of a preliminary plot trial also indicated that the concentration differences during a 15-min enclosure time were larger than 0.015 ppm, satisfying the criteria set out by Hutchinson and Mosier (1981) to reduce instrument error due to the standard deviation of the results from the gas chromatograph (the standard deviation of N_2O concentration determination was ±0.005 ppm). However, fluxes were measured immediately after application during the preliminary plot trial and they were measured 24 hrs after application during the full factorial study. Therefore, concentration differences were lower during the full factorial study, often falling below Hutchinson and Mosier's 0.015 ppm criteria. However, the measured fluxes were statistically significant based on the regression analysis and significant treatment effects were also observed so the 15-min enclosure time appeared sufficient. The low concentration differences did result in high uncertainties associated with the flux measurement (8-50% for CO_2, 9-55% for N_2O, >100% for CH_4, Appendix H).

After initial tests with the open port and a manometer showed no significant pressure fluctuations in the chamber at various ambient wind speeds, the open port was plugged with a semi-permeable foam membrane during gas sampling. After each sampling period was completed, the port was opened and a depth gauge was dropped into the port to measure the actual height of the deployed chamber. The chamber was rotated 90 degrees three successive times so a total of four depth measurements were collected. The average of the four depth measurements was used to calculate chamber volume.

The static chambers were tested on a calibration box which simulated carbon dioxide (CO_2) flux as described in Agnew et al. (2005). During these tests, the chambers underestimated the actual CO_2 flux by more than 50%. However, these laboratory tests simulated very low CO_2 fluxes (approximately 0.3 mg/m^2-s) while the fluxes observed

during the field tests were much higher, approximately 10 times higher than the simulated flux. Therefore, the field chamber measurements were likely more accurate than the calibration chamber measurements.

4.3.2 Experimental Design for Data Collection

Greenhouse gas emissions from surface and subsurface application of liquid and solid manure were measured on a plot scale, rather than full-scale field testing to control variables such as application rate and application method and type of manure. Liquid swine and dairy manures and solid swine, poultry and feedlot manures were surface applied and injected at three application rates with 3 replications in a randomized block design. Application rates (1X, 2X, 3X) were chosen to simulate one year, two year and three year agronomic rates based on N content. Details of the experimental design for the U of S Feedlot, Saskatoon Area and Humboldt Area plots in 2007 can be found in Chapter 3 (Odour Emissions from Manure Spreading). Additional GHG measurements were collected in 2007 from long-term solid and liquid manure and newly established solid manure application sites located near Dixon, SK. Refer to Tables 4.1 and 4.2 for details.

Table 4.1 Summary of GHG data collection in 2007.

Location	Type(s) of manure	Method of application	Application treatments
Dixon	Liquid swine	PAMI tanker truck	Long term liquid plots*
Dixon	Composted feedlot	Solid injection prototype	New solid plots*
Dixon	Composted feedlot	Solid injection prototype	Long term solid plots*
U of S Feedlot	Liquid dairy and solid feedlot	Simulated application	Surface and subsurface, 4 rates
Saskatoon area	Liquid swine and solid swine	Simulated application	Surface and subsurface, 4 rates
Humboldt area	Solid poultry	Solid injection prototype	Surface and subsurface, 4 rates

* Details for these plots listed in Table 4.2

Number of GHG samples collected:

56 flux measurements (all machine application—long term sites at Dixon)

123 flux measurements (99 simulated application, 24 machine application)

The Dixon data included emissions from a long-term liquid swine injection site (PAMI low disturbance injector tanker truck), a long-term solid feedlot application site where the manure was surface applied and incorporated (hand applied until 2007, solid manure injector prototype in 2007), and a new solid feedlot application site (solid manure injector prototype) where gaseous measurements were collected from the surface applied plots

only. The liquid plots included control treatments, application rate treatments, a water treatment and a broadcast + incorporation treatment. The solid plots included control treatments, application rate treatments and a delayed incorporation treatment. A summary of treatments for the Dixon sites are listed in Table 4.2. These plots and the manure application schedule were established in 1997 and accommodated a rotation of canola, wheat, flax, and barley. For this study, GHG samples were collected in the spring of 2007 from flax stubble 24 hrs after manure application.

Table 4.2 Summary of treatments for Dixon manure application sites.

Long-term liquid	Long-term solid	New solid
Control	Control	Control
Disturbed control	1X annually	1X annually
1X annually	2X every 2 years	2X annually
2X every 2 years	2X annually	3X annually
2X annually	4X every 3 years	
4X annually	4X annually	
1X water annually	1X annually delayed incorporation	
1X annually broadcast and incorporated		

4.3.3 Manure Application

For the Dixon plots and the Humboldt Area plots, full-sized application equipment (the PAMI liquid tanker truck and the PAMI solid prototype applicator) were used to apply the manure. Due to logistical constraints, the manure application was "simulated" by hand for the U of S Feedlot and Saskatoon Area plots.

Equipment details for machine applied plots and procedures for simulated application plots can be found in Chapter 3. The application rates used in the machine and simulated application plot trials are outlined in Tables 4.3 and 4.4, and the chemical properties of the manure used in these plots are in Tables 4.5 and 4.6.

Table 4.3 Liquid and solid manure application rates for machine application plots.

Rate	Solid (Mg/ha)	Liquid (m^3/ha)
1X	20	30
2X	40	60
3X	60	-
4X	80	120

Table 4.4 Liquid and solid manure application rates for simulated application plots.

Rate	Solid (Mg/ha)	Liquid (m^3/ha)
1X	20.2	56.1
2X	40.4	84.2
3X	60.6	112.2

Table 4.5 Manure chemical properties used in machine application plots.

	Total Solids (%)	NH_4 (kg/m^3)	Total N
Composted beef (long term plots)	n/a	0.05	4.79 kg/m^3
Composted beef (new solid plots)	n/a	0.042	4.99 kg/m^3
Liquid swine	n/a	1.8	2.07 kg/m^3
Solid poultry	46.4	3.25	17.3 kg/Mg

Table 4.6 Manure chemical properties used in simulated application plots.

	Total Solids (%)	Ammonia as N (kg/m^3)	Total N
Solid feedlot	38.2	n/a	8.3 kg/Mg
Liquid dairy	6.9	0.60[1]	2.5 kg/m^3
Solid swine	43.2	n/a	7.0 kg/Mg
Liquid swine	2.8	2.88	3.24 kg/m^3

[1]Value is lower than typical because liquid dairy manure was "generated" by taking fresh semi-solid manure directly from alley of barn and diluted with equal parts of water, and applied within 12 hours of mixing, resulting in little time for microbial activity and generation of NH_4-N.

For one randomized block experiment (liquid dairy), additional disturbed control plots were applied with a 1X (56.1 m^3/ha) rate of water to investigate whether the application of liquid promoted the generation of significant GHG's.

4.3.4 Soil Properties

All plots were located in wheat, flax or barley stubble and had no commercial fertilizer application after the crop was harvested the previous year. Soil samples were collected from each site on each day of emission sampling to provide data on basic soil characteristics. Samples were collected using a 10-cm soil probe from four locations immediately surrounding the plot site. Sub-samples were used for moisture content analysis by oven drying according to ASTM standards (D2216-05) and the remaining sample was dried and frozen for nutrient and particle size analysis. The bulk density approximation was based on published values for the texture class. The nitrogen, organic carbon and organic matter contents were analyzed by ALS Laboratory Group in Saskatoon, SK using standards outlined in Nelson and Sommers (1996) and Tiessen and

Moir (1993). A summary of the soil properties for the locations used in this study is presented in Table 4.7.

Table 4.7. Soil properties for data collection sites.

Site Location	Texture Class	Moisture Content Range (% d.b.)	Bulk Density (g/cm^3)	Nitrogen Content (% LECO-N)	Organic Carbon Content (%)	Organic Matter Content (%)
U of S Feedlot	Sandy loam	15.7 – 34.4	1.49	0.30	3.2	5.5
Saskatoon area	Loam	19.8 – 23.8	1.47	0.34	3.4	5.8
Humboldt	Clay loam	26.1 – 31.9	1.31	0.44	4.4	7.5
Dixon	Loam	n/a	1.29	0.47	3.2	5.4

4.3.5 Statistical Analysis

To calculate GHG flux using Equation 4.1, the rate of increase in concentration was determined using regression analysis. The fit of linear and quadratic models were analyzed by comparing the P values of the regression. If the P values for both regressions were greater than 0.15, the regression was deemed insignificant and the flux assumed to be zero. Of the significant fluxes, the regression model with the lowest P value was differentiated with respect to time to determine the slope of the regression at t = 0. This value was used as the $\Delta C/\Delta t$ term in Equation 4.1 to calculate gas flux. Details of the fluxes calculated from the significant and non-significant and linear vs. quadratic regressions can be found in Appendix G.

The CO_2, N_2O and CO_2 equivalent (CO_2-e) fluxes were highly variable with many small values including zeros. Based on the Kolmogorov-Smirnoff test (Greenberg, 2006), the CO_2, N_2O and CO_2-e fluxes were not normally distributed ($P<0.05$) so non-parametric statistical analyses were employed, as in Bergstrom et al. (2001). The CH_4 fluxes were normally distributed ($P>0.150$).

For the non-normally distributed fluxes, individual flux values were assumed to be outliers if they fell beyond three interquartile ranges from the upper quartile (Pett, 1997).

Since the data were highly variable and dependent on the treatments, quartiles and interquartile ranges were calculated for each individual treatment to identify the outliers. The N_2O and CO_2 outliers were reintroduced for the CO_2-e calculation and CO_2-e outliers were assessed individually.

The Kruskal Wallis non-parametric test (Greenberg, 2006) was used to determine significance of treatment effects on N_2O, CO_2 and CO_2-e fluxes. Treatment effects on CH_4 fluxes were analyzed using ANOVA. Treatments were considered to have a significant effect on the flux when the P value was less than 0.05 to provide a high level of confidence (95%). All statistical analyses were performed using Minitab software (version 15) (Greenberg, 2006).

Although non-parametric statistical analysis deals with median values to determine significance, all graphs and tables list treatment means and standard errors for easier interpretation. Outliers were treated as missing data and insignificant fluxes were considered as zero.

4.4 Results

Due to the differences among treatments and application rates between the factorial experiment (U of S Feedlot, Saskatoon Area and Humboldt Area plots) and the long term experiment (Dixon plots), the GHG emission results were analyzed independently and will be presented separately.

Most of the plots produced significant N_2O and CO_2 fluxes, but very few CH_4 fluxes had significant regressions for the rate of increase in gas concentration in the headspace. Furthermore, the significant CH_4 fluxes were very low and varied between positive (emission of CH_4) and negative (uptake or CH_4 oxidation) values. Therefore, the carbon dioxide equivalent (CO_2-e) calculation excluded the CH_4 fluxes and accounted for N_2O

(with a global warming potential of 310) and CO_2 only. Additional graphical and numeric summaries of the GHG fluxes are in Appendix I.

4.4.1 Factorial Experiment Results

Using the regression analysis outlined in Section 3.5, 95 of the 123 N_2O fluxes were significant, 107 of the 123 CO_2 fluxes were significant and 45 of the 123 CH_4 fluxes were significant. The treatment effects (liquid vs. solid, surface vs. injected, application rate) on N_2O, CH_4, CO_2 and CO_2-e fluxes are presented separately, following a discussion of outliers and control fluxes.

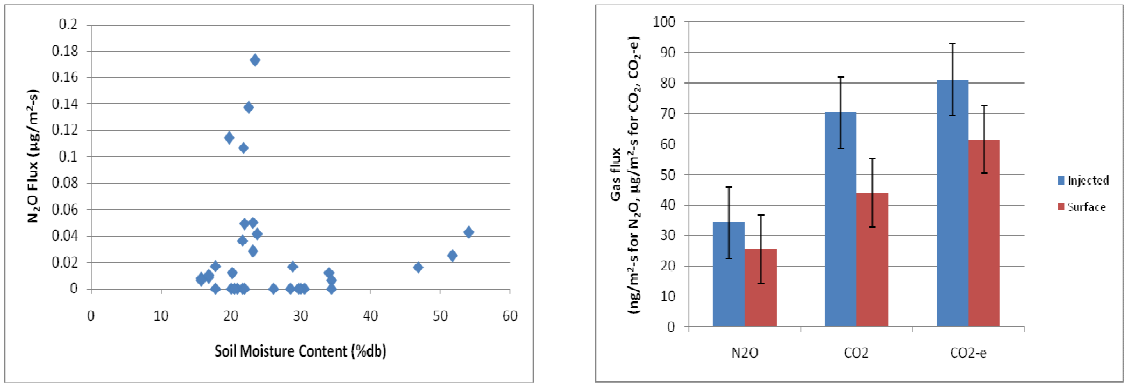
4.4.1.1 Outliers

Although the data were highly variable, outliers can affect data analysis and conclusions. Therefore, outliers were excluded from the statistical analysis. There were 11 N_2O flux outliers (out of 95 significant fluxes), 3 CO_2 flux outliers (out of 107 significant fluxes) and 3 CO_2-e flux outliers (out of 117 significant fluxes). These outlier values and the rationale for their exclusion are included in Appendix I.

4.4.1.2 Control Fluxes

Microbial activity in soil is highly dependent on soil moisture content, so it follows that GHG emissions may be dependent on soil moisture content. The scatter-plot describing the relationship between soil moisture content and N_2O emissions for the simulated application plot data are presented in Figure 4.2a (scatter-plots for effect of soil moisture on CO_2 and CO_2-e are in Figure I.1 in Appendix I). Based on these data, there doesn't appear to be a trend between moisture content and CO_2-e fluxes measured 24 hours after application, but the maximum fluxes appear to be confined to a small range of moisture contents (20-25% db) which corresponded to a WFPS range of 44 to 51% for these soils (average wet bulk density 1.42 Mg/m^3).

Since the fluxes may have also been influenced by the amount of soil disturbance due to injection, the fluxes were compared between disturbed and undisturbed control plots. While emissions from the disturbed control plots tended to be higher than emissions from the undisturbed control plots, the difference was not significant for any of the gases measured (P = 0.243 for N_2O, 0.052 for CO_2, 0.775 for CH_4 and 0.131 for CO_2-e, Figure 4.2b). The low P value for CO_2 indicates that soil disturbance tended to increase CO_2 flux, likely due to increased soil respiration due to enhanced soil microbe exposure to the atmosphere.



(a) (b)

Figure 4.2. Control fluxes (a) scatter plot of N_2O emissions (µg/m^2-s) versus oven dry basis soil moisture content (%), (b) effect of soil disturbance on background fluxes.

The results from the disturbed control plots applied with a 1X rate of water showed that the emissions from these disturbed control plots were higher but not significantly different from the other control plots in that block (P = 0.146, data not shown). This suggests that the moisture applied when injecting manure did not affect the microbial population enough to alter the GHG emissions occurring one day after manure application.

The background N_2O fluxes varied significantly among locations (U of S Feedlot < Humboldt Area < Saskatoon Area, P = 0.003). This made it necessary to calculate a "manure induced" N_2O flux to account for the varying N_2O emitted from bare soil when analyzing the treatment effects on the N_2O flux. Since the background N_2O fluxes varied only with location, the data were pooled by location to determine overall background N_2O flux. These values are summarized in Table 4.8. The CO_2, CH_4 and CO_2-e fluxes

from the control plots did not vary by location (P = 0.243, 0.335 and 0.194, respectively). The overall background CO_2, CH_4 and CO_2-e fluxes were 58.0, 0.0387 and 71.8 μg/m^2-s, respectively.

Table 4.8. Summary of background N_2O fluxes by location (μg/m^2-s). Numbers in brackets represent the standard error of the mean value.

Location	Background N_2O Flux	
	n	Mean
U of S Feedlot	13	0.0052 (0.00158)
Saskatoon Area	11	0.0679 (0.0168)
Humboldt Area	6	0.0168 (0.0066)

4.4.1.3 N_2O Fluxes

The treatment effects on N_2O fluxes were analyzed for each location separately due to the varying background N_2O fluxes at each location. The N_2O fluxes from the Saskatoon Area plots (liquid and solid swine manure) were significantly higher than the N_2O fluxes from the other two locations. Figure 4.3 is a graphical summary of the treatment effects on the N_2O fluxes from all three locations.

Injection significantly increased N_2O fluxes from all locations (P=0.007, 0.001, 0.000 for U of S, Saskatoon Area and Humboldt Area, respectively, Figure 4.3a). N_2O fluxes from liquid manure were significantly higher than from solid manure at the U of S (P=0.002) and Saskatoon Area (P=0.007) locations (only solid manure was spread at Humboldt Area location, Figure 4.3b). Interestingly, application rate had no significant effect on N_2O flux (P = 0.585, 0.447, 0.477 for the U of S, Saskatoon Area and Humboldt Area, respectively), although the mean N_2O flux increased with application rate at most sites (Figure 4.3c). This indicates that there was no difference in N_2O flux between the control and manured plots (median values for N_2O flux for 0X, 1X, 2X and 3X rates for Saskatoon Area plots were: 0.049, 0.061, 0.028, and 0.111 μg/m^2-s, respectively).

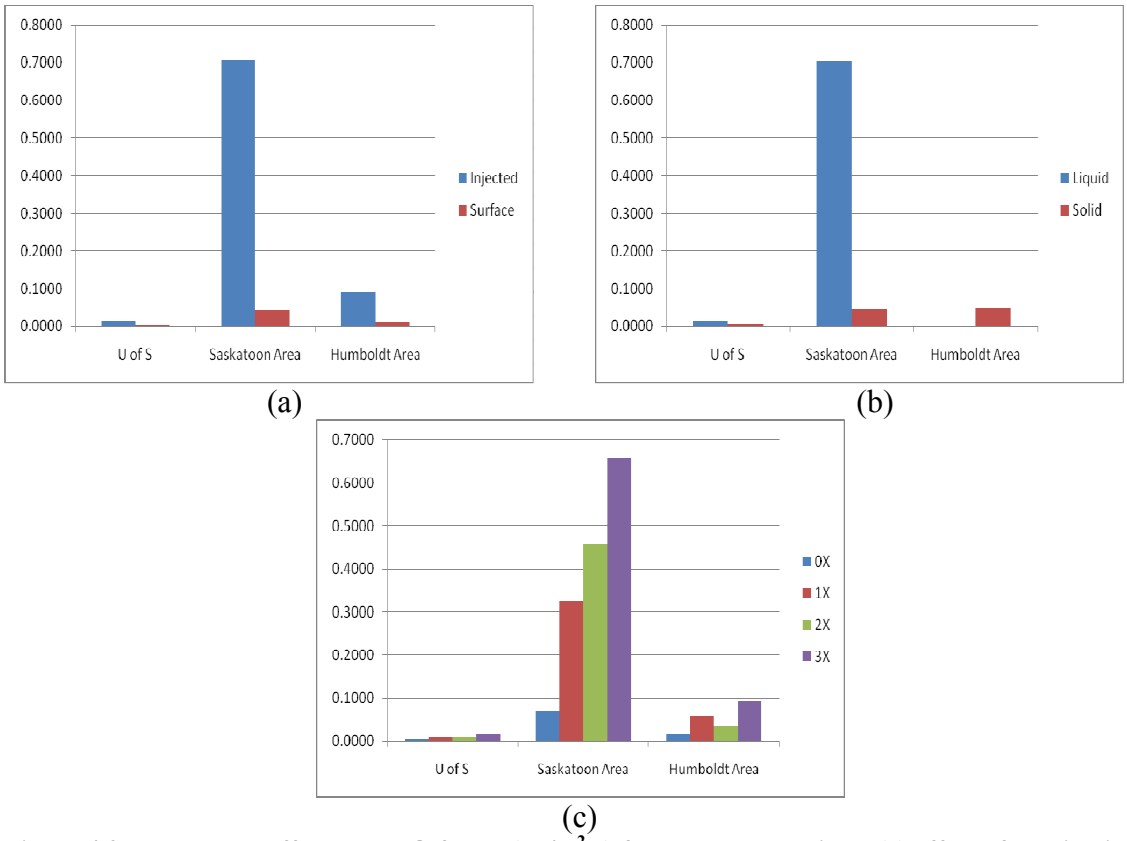


Figure 4.3. Treatment effects on N_2O fluxes (µg/m^2-s) for all three locations. (a) effect of application method, (b) effect of manure type, and (c) effect of application rate. Data does not include background correction.

Because the background N_2O fluxes varied by location, the "manure induced" N_2O flux was also calculated by subtracting the mean background flux of each location from the total fluxes obtained at that location. Analysis of these manure induced fluxes showed that injection significantly increased the N_2O from the manure (P=0.000) and the manure induced N_2O fluxes were higher from liquid manure applications than solid manure applications (P=0.025). In fact, the mean manure induced N_2O flux from the surface applications and solid manure showed N_2O uptake by the soil while injected applications and liquid manure showed N_2O emission (refer to Table 4.9). The solid feedlot, solid swine and liquid dairy applications had negative manure induced N_2O fluxes while the solid poultry and liquid swine had positive manure induced N_2O fluxes (refer to Table 4.9). Similar to the absolute N_2O flux analysis above, the application rate did not affect manure induced N_2O fluxes (P=0.243). The poultry manure generated significantly higher manure induced N_2O fluxes than the other solid manures.

Table 4.9. Summary of manure induced N_2O fluxes (µg/m^2-s). Separate analyses were carried out for the overall data, solid manure and liquid manures.

		n	P value	Mean	Std Err
Overall	Injected	58	0.000	0.2505	0.0805
	Surface	52		-0.0305	0.0052
	Liquid	46	0.025	0.2870	0.1010
	Solid	64		-0.0040	0.0096
	0X	30	0.243	-0.0170	0.0066
	1X	28		0.1019	0.0726
	2X	26		0.1581	0.0917
	3X	26		0.2490	0.1420
Solid	Injected	33	0.015	0.0195	0.0167
	Surface	31		-0.0291	0.0064
	Feedlot	20	0.000	-0.0078	0.0024
	Poultry	21		0.0507	0.0216
	Swine (S)	23		-0.0506	0.0108
Liquid	Injected	25	0.000	0.5550	0.1690
	Surface	21		-0.0326	0.0091
	Dairy	24	0.613	-0.0003	0.0114
	Swine (L)	22		0.6000	0.8960

4.4.1.4 CO_2 Fluxes

Since background CO_2 fluxes did not vary by location, the statistical analysis was performed on the overall pooled data. The overall analysis showed that injection significantly increased CO_2 flux (P=0.003, Figure 4.4a) and fluxes from liquid manure were higher than from solid manure (P=0.000, Figure 4.4b). The CO_2 flux increased with application rate. Although the differences among the 1X, 2X and 3X application rates were not significant, CO_2 fluxes from the manured plots were significantly higher than from the control plots (P=0.021, Figure 4.4c). The poultry manure plots generated the highest fluxes of the solid manures while the liquid swine plots generated the highest CO_2 fluxes of the liquid manures (Figure 4.4d).

The effects of application method and rate were analyzed separately for liquid and solid manure to determine if there were any interesting trends. Injection seemed to increase the CO_2 flux more for liquid manure than solid manure and fluxes from the injected and liquid plots increased more rapidly with higher application rates than fluxes from surface applied and solid manure plots. These plots of interactions are shown in Figure I.2 in Appendix I.

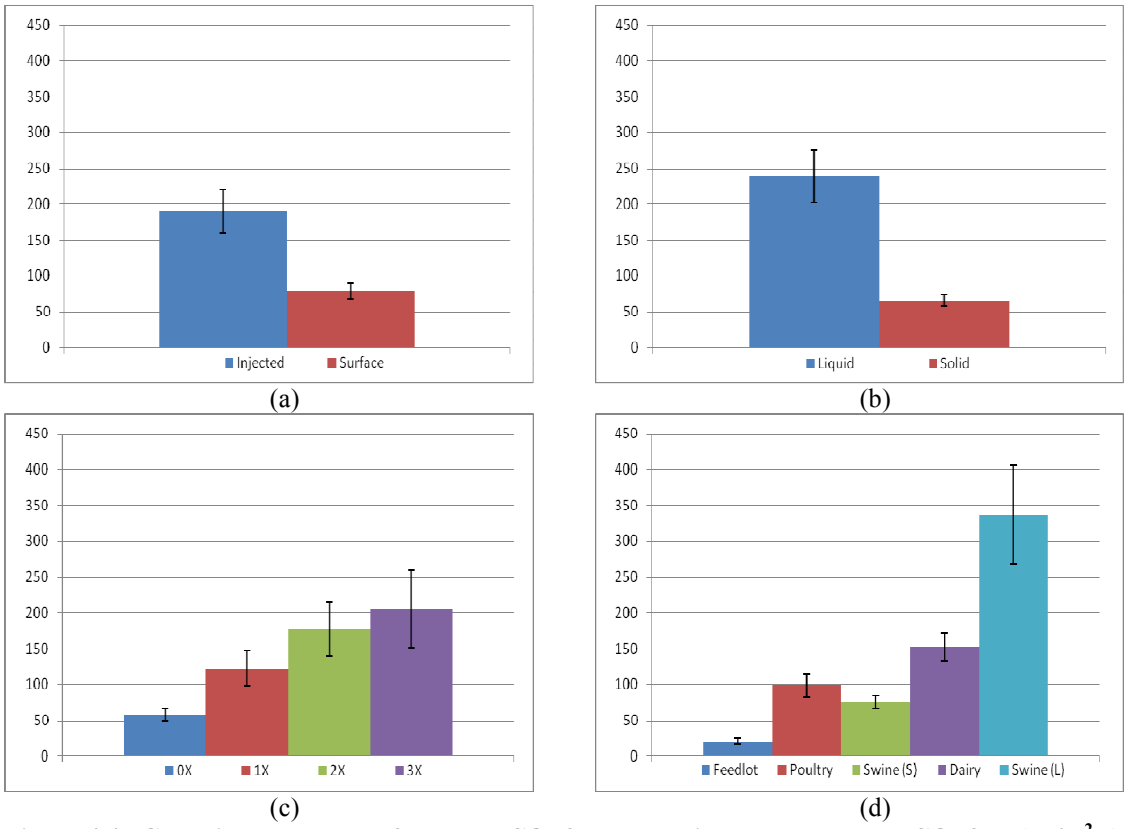


Figure 4.4. Graphical summary of absolute CO_2 fluxes. Vertical axes represent CO_2 flux ($\mu g/m^2$-s). Solid bars and line error bars correspond to average values and standard errors of the means, respectively. (a) Effect of application method, (b) effect of manure type, (c) effect of application rate, (d) effect of manure species.

4.4.1.5 CH_4 Fluxes

Only 45 of the 123 CH_4 fluxes had a significant regression analysis, so non-significant fluxes were treated as missing data, not as zero as was done in the CO_2 and N_2O flux analysis. So many CH_4 fluxes were non-significant that to treat them as zero resulted in highly skewed data (Table I.10 in Appendix I summarized CH_4 data with non-significant fluxes as zero). The methane fluxes varied between emission (positive) and uptake (negative) but there were no significant differences among any of the treatments. The CH_4 fluxes with significant regression analyses are summarized in Table 4.10.

Plots applied with solid manure tended to oxidize CH_4 (negative flux) while plots applied with liquid manure emitted CH_4. There was a trend for the injected plots to have lower CH_4 fluxes and application rate had no obvious trend on CH_4 flux. The feedlot and

poultry manures tended to oxidize CH_4 as well, whereas the dairy and both liquid and solid swine manures emitted CH_4.

Table 4.10. Summary of CH_4 fluxes with significant regression analyses. Mean and standard error of fluxes have units of µg/m^2-s.

	n	P value	Mean	Std Err
Liquid	20	0.249	0.0488	0.0227
Solid	25		-0.0109	0.038
Injected	24	0.676	0.012	0.0367
Surface	21		0.0198	0.0292
0X	13	0.308	0.0387	0.0422
1X	13		-0.0582	0.0424
2X	9		0.0414	0.0513
3X	10		0.0583	0.0528
Dairy	15	0.155	0.0585	0.0257
Feedlot	2		-0.3759	0.0476
Poultry	11		-0.0265	0.0359
Swine (L)	5		0.0196	0.0507
Swine (S)	12		0.0642	0.0538

4.4.1.6 CO_2-e Fluxes

To account for the high global warming potential of N_2O (310 times that of CO_2), the carbon dioxide equivalent (CO_2-e) values were calculated (Table 4.11). Since the CH_4 fluxes were low with few significant fluxes, CH_4 was excluded from the CO_2-e calculation. Therefore, CO_2-e equalled the N_2O flux multiplied by 310 plus the CO_2 flux.

Since the CO_2 fluxes were more than double the carbon dioxide equivalent N_2O fluxes (overall mean CO_2 flux = 137.5 µg/m^2-s and overall mean carbon dioxide equivalent N_2O flux = 51.4 µg/m^2-s), the CO_2-e flux trends and treatment significances were very similar to the CO_2 flux trends (refer to Figure 4.4). The treatment effects on CO_2-e fluxes are shown in Figure I.3 in Appendix I.

When the effect of injection on CO_2-e fluxes was analyzed for each manure species, injection significantly increased CO_2-e fluxes from liquid swine and solid poultry manure (P=0.002, 0.017 respectively). Injection tended to increase CO_2-e fluxes from solid swine manure (P=0.074) while injection had no significant effect on feedlot and liquid dairy manure (P=0.621 and 0.312, respectively). A summary of the CO_2-e flux values for the overall data, solid manure and liquid manure is presented in Table 4.11.

Table 4.11. Summary of CO_2-e flux data (µg/m^2-s).

		N	P value	Mean	Std Err
Overall	Injected	61	0.001	279.6	54.4
	Surface	55		86.1	11.6
	Liquid	49	0.000	342.7	64.9
	Solid	67		74.7	9.1
	0X	32	0.054	71.8	10.4
	1X	29		163.4	45.9
	2X	29		240.2	63.3
	3X	26		299.6	99.0
Solid	Feedlot	23	0.000	23.0	4.6
	Poultry	21		109.7	20.9
	Swine (S)	23		94.3	12.3
	Injected	34	0.030	99.6	15.5
	Surface	33		49.0	7.2
	0X	17	0.578	49.4	6.2
	1X	17		60.7	15.3
	2X	17		104.9	24.9
	3X	16		84.2	19.7
Liquid	Dairy	26	0.034	157.6	20.6
	Swine (L)	23		552.0	124.0
	Injected	27	0.009	506.0	107.0
	Surface	22		22.3	22.3
	0X	15	0.002	97.3	19.4
	1X	12		308.9	95.9
	2X	12		432.0	133.0
	3X	10		644.0	120.0

The contributions of N_2O to CO_2-e as a percentage for the three locations are summarized in Table 4.12. The contribution of N_2O to CO_2-e was analyzed by calculating the percentage of CO_2-e that was made up of carbon dioxide equivalent N_2O. Treatments where the CO_2 fluxes were insignificant (zero) were excluded. These percentages were analyzed to determine treatment effects. Again, because the background N_2O flux varied by location, the contributions of N_2O to CO_2-e were analyzed separately for each location. Injection significantly increased the contribution of N_2O to CO_2-e at all locations (P=0.004 in Humboldt Area plots, 0.002 in Saskatoon Area plots and 0.045 in U of S feedlot plots). The contribution of N_2O to CO_2-e tended to be higher from liquid manure applications, but there were no significant trends (P=0.073 in Saskatoon Area plots and 0.222 in U of S Feedlot plots). Application rate had no effect on the percentage contribution of N_2O to CO_2-e.

Table 4.12. Contributions of carbon dioxide equivalent N_2O to overall CO_2-e, expressed as a percentage.

Location	Treatment	n	P-value	Mean (%)	Std Err (%)
U of S Feedlot	Injected	21	0.045	5	1
	Surface	20		3	1
	Liquid	26	0.222	3	1
	Solid	15		5	2
Saskatoon area	Injected	23	0.002	29	3
	Surface	22		14	4
	Liquid	22	0.073	27	4
	Solid	23		16	2
Humboldt area	Injected	11	0.004	21	3
	Surface	10		9	3

4.4.1.7 Specific Fluxes

Since the total N application rates were not the same for the different manure types and species, specific GHG flux rates were calculated by dividing the flux values by the total N application rates outlined in Table 4.13. Specific flux values were calculated for all 3 greenhouse gases based on application of total N. Only the results of CO_2-e per kg total N are presented in Figure 4.5. The specific flux trends for N_2O and CO_2 can be found in Figures I.4 and I.5 in Appendix I.

Table 4.13. Summary of actual N application rates for factorial experiment plots.

		kg N-tot/ha		
Manure	**Total N**	**1X**	**2X**	**3X**
Feedlot	8.3 kg/Mg	168	335	503
Swine (S)	7.0 kg/Mg	141	283	424
Poultry	17.3 kg/Mg	350	700	1050
Dairy	2.5 kg/m^3	140	211	281
Swine (L)	3.2 kg/m^3	182	273	364

Similar to the absolute CO_2 and CO_2-e flux analyses, specific CO_2-e fluxes (Figure 4.5) were significantly higher from the injected plots (P=0.005) and from the liquid manure (P=0.000). Again, there was no statistical difference among the 1X, 2X and 3X application rates (P=0.428). This suggests that the rate of increase of absolute GHG flux with application rate is proportional to the rate of increase of applied N. In terms of specific CO_2-e flux, the solid swine manure emitted the most GHG's of the solid manures while the liquid swine manure emitted the most GHG's of the liquid manures.

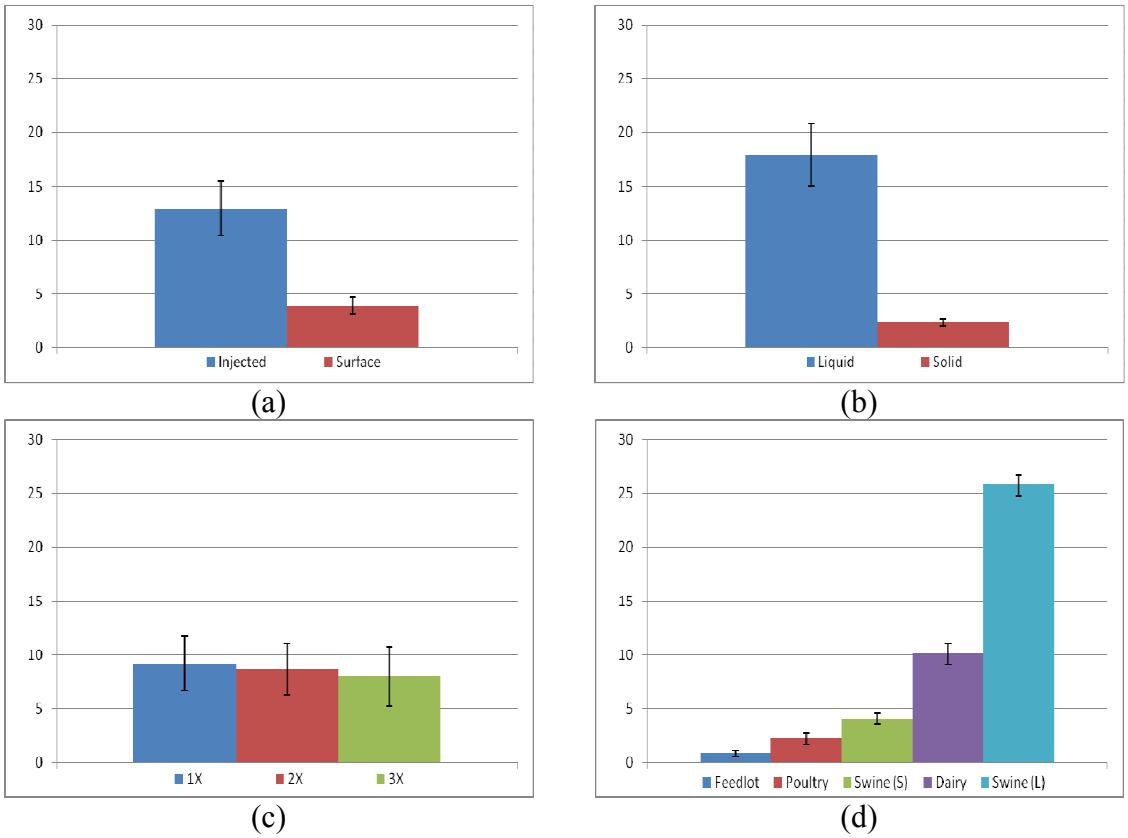


Figure 4.5. Treatment effects on mean specific CO_2-e fluxes (mg/kg N applied-s). Solid bars and line error bars correspond to average values and standard errors of the means, respectively. (a) Effect of application method, (b) effect of manure type, (c) effect of application rate, and (d) effect of manure species.

4.4.2 Long Term Experiment Results (Dixon Results)

Comparisons between liquid and solid manure and surface and subsurface applications were difficult to make with the Dixon data since the experiment was not designed to make these comparisons. The goal of the Dixon experiment was to assess the long-term effects of repeated manure applications. However, a few valid conclusions can be drawn from these data.

There were many fluxes that could not be distinguished from zero (insignificant regression) but no outliers in the Dixon flux data. Of the 56 fluxes measured, 29, 49 and 23 of the N_2O, CO_2 and CH_4 fluxes had significant regressions, respectively. Generally, absolute emissions from the Dixon sites were lower than from the factorial plot sites,

despite the fact that the Dixon site included repeated solid and liquid manure application treatments. However, some of the plots from the long term site included treatments that were applied every 2 or 3 years, but not in the year the fluxes were measured. This resulted in the collection of more samples from plots that had received no manure than in the factorial experimental design. Furthermore, the nitrogen application rates were lower in the Dixon plots (Table 4.14) compared to the factorial experiment plots (Table 4.13).

Table 4.14. Summary of actual N application rates for Dixon plots.

	Total N	kg N-tot/ha			
Manure	**kg/m^3**	**1X**	**2X**	**3X**	**4X**
Liquid swine	2.1	68	136	-	272
Long-term solid feedlot	4.79	73	146	-	292
New solid feedlot	4.99	100	200	300	-

A comparison of overall absolute fluxes from long term sites and the factorial experiment plots is shown in Table 4.15.

Table 4.15. Comparison of overall mean fluxes from Dixon and factorial (all other locations) experiments. All fluxes are in µg/m^2-s. Numbers in brackets represent the standard error of the mean.

	N_2O Flux		CO_2 Flux		CH_4 Flux	
	Dixon	**Factorial**	**Dixon**	**Factorial**	**Dixon**	**Factorial**
Liquid	0.0456	0.344	144	238.8	-0.0027	0.0488
	(0.0139)	(0.104)	(27.8)	(36.3)	(0.0196)	(0.0227)
Solid	0.01090	0.03371	26.5	65.5	-0.1300	-0.0109
	(0.00606)	(0.00589)	(7.62)	(7.48)	(0.0172)	(0.038)
0X	0.00714	0.03051	58.2	58.0	-0.0503	0.0387
	(0.00596)	(0.00813)	(23.3)	(7.94)	(0.0477)	(0.0422)

The magnitudes of the specific fluxes from the Dixon plots were comparable to the specific CO_2-e fluxes in the factorial experiment (Figure 4.5). The specific CO_2-e fluxes from the long-term liquid plots at Dixon ranged from 5 mg/kg N-s for the 2X injected treatment to 60 mg/kg N-s for the 1X incorporated treatment. The new solid feedlot plots yielded specific CO_2-e fluxes below 1 mg/kg N-s while the long-term solid feedlot plots had specific CO_2-e fluxes that ranged from 1 to 5 mg/kg N-s.

4.4.2.1 Treatment Effects on N_2O Flux

Injection did not appear to affect N_2O flux from the plots applied with a 1X rate of liquid swine manure compared to the same rate when it was broadcasted and incorporated (P=0.513). However, the 4X liquid rate had significantly higher N_2O fluxes than all other liquid treatments (P=0.037). The 2X2 (a 2X rate applied every 2 years, no manure applied the year the fluxes were measured) plot appeared to have lower N_2O fluxes than the control plots. Refer to Figure 4.6 for a summary of the N_2O fluxes from liquid manure treatments.

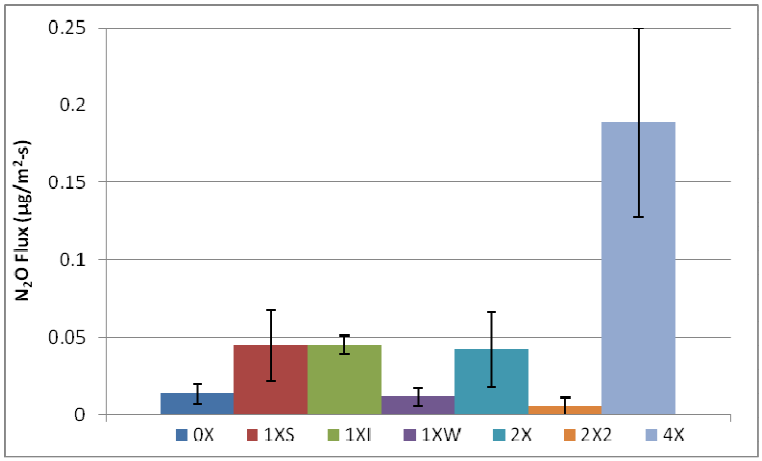


Figure 4.6. Summary of treatment effects on N_2O fluxes from liquid manure treatments in Dixon experiment. 0X represents control (no manure) plots, 1XS are the annually surface applied and incorporated plots, 1XI are the annually injected plots, 1XW are the annual water injected plots, 2X are the annually injected plots, 2X2 are the injected plots applied every two years (no manure in year of flux measurement) and 4X are the annually injected high rate plots.

There were no differences between the overall N_2O fluxes from the long term and new solid plots (P=0.454) and application rate had no effect on N_2O fluxes from either the long term or new solid plots (P=0.618 for new plots, P=0.454 for long term plots, data not shown). As was the case for the liquid plots, there were no significant differences between the control plots and multi-year application rate plots, indicating that high rate applications of both solid and liquid manure appeared to have no residual effect on N_2O fluxes in a non-application year. There was also no difference between the 1X surface application with immediate incorporation and 1X delayed incorporation of solid manure treatments (data not shown).

4.4.2.2 Treatment Effects on CO_2 Flux

These data indicate that injection resulted in lower CO_2 fluxes compared to surface application and incorporation of 1X rate of liquid swine manure. In fact, the 1X surface application and incorporation of liquid manure was significantly higher than all the other liquid treatments (P=0.040). Again, the annual 4X rate resulted in high emissions whereas 2X annual and 2X semi-annual rates were not different from the control plots. Refer to Figure 4.7 for a summary of the CO_2 fluxes from the liquid manure treatments.

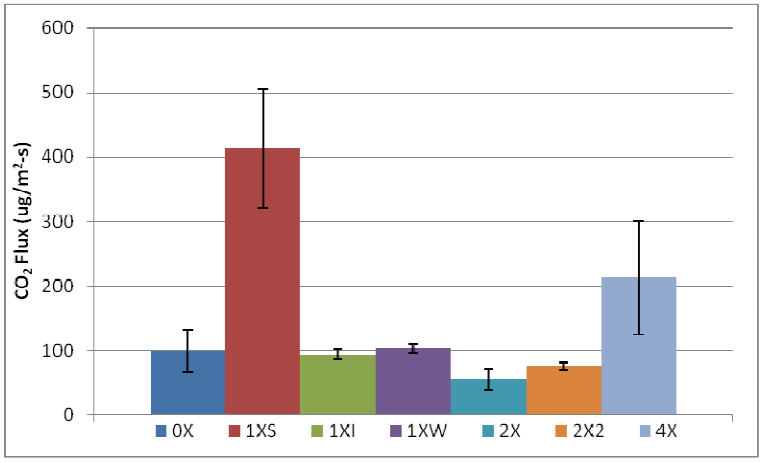


Figure 4.7. Summary of treatment effects on CO_2 fluxes from liquid manure treatments in Dixon experiment. Notations are the same as those defined in Figure 4.6.

The long term solid plots had an overall higher CO_2 flux than the new solid plots (P=0.000), but application rate had no effect on the CO_2 flux from either set of plots (P=0.379 for new plots and 0.254 for long term plots, data not shown). There did not appear to be a difference in fluxes between the immediate and delayed incorporation solid 1X plots (P=0.688). The 4X rate of solid manure applied every 3 years seemed to have a higher CO_2 flux in the non-application year than the control and 2X rate applied every 2 years (P=0.060, data not shown).

4.4.2.3 Treatment Effects on CH_4 Flux

While there was no difference in CO_2 and N_2O fluxes between liquid and solid manure plots, the solid manure plots had a significantly lower CH_4 flux than the liquid manure plots (P=0.000, data not shown). Since fluxes from both solid and liquid plots were negative, this suggests that soil applied with solid manure becomes a better CH_4 sink.

There were no other significant differences in CH_4 flux among treatments (data not shown).

4.5 Discussion

4.5.1 Effect of Application Method and Manure Type on GHG Emissions

Not unexpectedly, injection of manure increased overall CO_2-e emissions measured 24 hrs after application. The CO_2-e fluxes from the injected treatments were 3.2 times higher than CO_2-e fluxes from the surface treatments (specific CO_2-e flux was also 3.2 times higher from injected plots). While both CO_2 and N_2O emissions significantly increased with injection, the increase in N_2O flux was more pronounced. The overall mean CO_2 flux from the injected plots was 2.5 times higher than from the surface plots (median specific CO_2 flux increased by 2 times) while the overall mean N_2O flux from the injected plots was 13.5 times higher than from the surface plots (median specific N_2O flux was 5 times higher and mean manure induced flux was 10 times higher). This suggests that the enhanced microbial decomposition and increased CO_2 respiration due to increased contact between microbes and substrates under the soil surface is not entirely responsible for the increased emissions due to injection. When manure is placed under the surface, soil is likely to become partially or fully anaerobic due to reduced diffusion rates and rapid microbial activity that depletes the available oxygen very soon after application. Microbes that degrade organic material in anaerobic or partially anaerobic conditions then use nitrate as a terminal electron acceptor and produce more N_2O through denitrification than microbes that degrade organic material in aerobic conditions (refer to Chapter 2). Although the final product of denitrification is an inert gas (N_2), incomplete denitrification can result in a significant net emission of N_2O. Incomplete denitrification can be a result of carbon deficiency (not enough substrate for denitrifier activity) or high diffusion rates resulting in gases reaching the atmosphere before denitrification is complete.

The enhanced microbial dynamics due to manure injection is further demonstrated by the correlations between CO_2 and N_2O fluxes, shown in Figure I.6 in Appendix I. While the correlation coefficient value (square root of the R^2 value) was low in most cases (0.157 for liquid swine surface), some treatments had correlation coefficients as high as 0.92 (liquid swine injection). All treatments except the surface-applied solid feedlot plots had positive correlations and the injected treatments had noticeably higher correlation coefficients than the surface treatments. This means that even when the conditions promote high N_2O flux, the CO_2 flux was also high, particularly for the injected plots. Since aerobic microbes are responsible for mineralization and oxidation of C compounds to CO_2, it's possible that the N_2O generated from manure injection is mainly due to aerobic denitrification.

Manure injection appeared to have very little impact on CH_4 fluxes measured 24 hrs after application. This was likely due to the fact that the majority of CH_4 emissions from manure spreading are from the volatilization of CH_4 already in the manure and occur within 12 hrs after application (Chadwick et al., 2000, Chadwick and Pain, 1997, Weslien et al., 1998). In some cases, methanogens may produce CH_4 under the soil due to the availability of nutrients and the anaerobic conditions, but that process was not observed in this study. It is likely that the redox potential does not drop low enough for methanogensis to begin. In fact, injected manures had slightly lower CH_4 flux rates than surface applied manures. Since methanogens are strict anaerobes and conditions are unlikely to become completely anaerobic in the soil matrix (except for microsites), it is unlikely to see significant CH_4 production after manure application.

Since solid manure injection requires specialized equipment, most subsurface applications of solid manure are achieved through incorporation. Provided the manure is incorporated immediately after application, the microbial activity beneath the soil is likely to be similar for both subsurface application techniques, suggesting that incorporation of solid manure will also increase GHG fluxes measured 24 hrs after application compared to surface applications. One study directly compared N_2O fluxes from injection and incorporation of liquid manure (Weslien et al., 1998). Although the

results were not statistically significant, the authors noted higher fluxes from the incorporation method than the injection method, similar to the CO_2 flux observations at the Dixon site in this study. Weslien et al. (1998) postulated that harrowing spread around the manure under the soil, creating more anaerobic microsites that resulted in incomplete denitrification and N_2O emissions while injection seemed to result in complete denitrification, producing N_2 instead of N_2O. On the other hand, Perala et al. (2006) found that injection of slurry resulted in higher N_2O emissions but lower CH_4 emissions than incorporation of manure and the results from this study found no difference in N_2O flux between injection and incorporation of liquid swine manure.

While previous research has sometimes found few significant trends in the effect of manure application on GHG fluxes, most previous researchers have noted significantly higher fluxes from liquid manure applications than solid manure applications in the short term. Results from this study also indicate that GHG fluxes measured 24 hours after application from liquid manure were higher than from solid manure (CO_2-e fluxes were 4.5 times higher and specific CO_2-e fluxes were 7.5 times higher). The manure induced N_2O flux was almost 100 times higher from liquid applications than from solid applications while the CO_2 and specific CO_2 fluxes were 3.5 and 7.5 times higher, respectively. Soils that received liquid manure applications also tended to have higher CH_4 fluxes than the soils applied with solid manure.

Because liquid manures are usually stored under anaerobic conditions, liquid manure contains higher levels of water-soluble carbon and nitrogen (Banham and Haugen-Kozyra, 2004; Moolecki et al., 2002), leading to increased rates of nitrification and denitrification after it is applied to the soil. In solid manure, nutrients are physically protected from the attack of decomposers by the solid matrix (Rochette et al., 2004). Additionally, the N and C in solid manures tend to be in organic forms that release available N very slowly (Qian and Schoenau, 2002). The low NH_4-N content in solid manure results in less nitrification to NO_3 and subsequent denitrification to N_2O. In fact, feedlot manure addition can actually initially immobilize inorganic N (Jeff Schoenau, personal communication, 11/09), as suggested by the negative manure induced N_2O flux

for solid manure (Table 4.9). However, due to the inclusion of bedding material such as straw, solid manures tend to have high total C contents which can be mineralized to CO_2 over time. This abundance of C in solid manure may result in higher cumulative emissions from solid manure applications, as was observed in Loro et al. (1997). In fact, many researchers have noted that available C content is as important as NO_3 and O_2 concentrations in driving the N transformation process (Myrold and Tiedje, 1985; Hojberg et al., 1994 in: Rochette et al., 2000b). One exception was the suggestion by Chadwick et al. (1999) that switching from straw-based cattle systems to slurry based systems would reduce N_2O emissions. They stated that encouraging anaerobic conditions during storage would actually reduce N_2O emissions because anaerobic conditions inhibit nitrate production and hence, formation of N_2O after application. However, when land applied, rapid nitrification of NH_4 accumulated during anaerobic storage may result in a large pulse of N_2O produced as noted in this study. Interestingly, switching from straw based systems may actually abate N_2O emissions due to the reduction in total C content, not the inhibition of NO_3 production.

As discussed in the literature review (Sections 4.2.2.2 and 4.2.2.3), all of the previous research that also reported increased emissions after subsurface application used liquid manure or slurry. The effect of injection on emissions from solid manure has not been investigated. When the results from the solid manure applications were analyzed separately from the liquid manure applications, the N_2O flux (mean flux, median specific flux and manure induced flux) were significantly higher from the injected plots for both manure types, but the magnitude of increase was much higher from the liquid plots. For example, the manure induced N_2O flux from the solid plots was 2.67 times higher due to injection while the manure induced N_2O flux from the liquid plots was 19 times higher due to injection. Therefore the liquid manure with more N in ammonium form coupled with the addition of liquid that can increase WFPS is more likely to be affected by placement strategy when it comes to N_2O emissions.

The results from the different manure species indicated that injection significantly increased N_2O fluxes from the liquid swine and solid poultry manures, likely due to their

higher NH_4 contents. The ammonium probably rapidly nitrified to NO_3 which was then susceptible to denitrification and transformation to N_2O. Since both the nitrification and denitrification processes are sources of N_2O (Firestone and Davidson, 1989), this rapid nitrification is a significant source of N_2O from those manures. Interestingly, injection significantly increased CO_2 fluxes from only the liquid swine and solid poultry manures as well, suggesting that the microbial activity and decomposition were higher in the soil after the application of those manures. The differences between surface fluxes and injected N_2O fluxes were too small and variable to determine significance for the other manure species. The recalcitrant nature of some cattle manures and composts (Qian and Schoenau, 2002) could explain a reduced effect of placement for the feedlot manure.

In order to fully assess the effect of application method and manure type on total GHG emissions, fluxes should be monitored over several weeks or months after application. Alternatively, mechanistic models that predict nutrient transformations may be used to simulate the effects of varying environmental conditions associated with different application techniques and manure types. This way, the entire effect of applying liquid or solid manure and the placement of the manure on total GHG emissions can be assessed. Indeed, part of the reason for variable results reported in the literature is due to the different time scales used in the assessment. Previous researchers have monitored fluxes anywhere from 72 hrs up to 6 months after application (Lovanh et al., 2008; Sistani et al., 2008; Weslien et al., 1998; Perala et al., 2006; Flessa and Beese, 2000; Wulf et al., 2002b) and up to one year after application (Chang et al., 1998; Goodroad et al., 1984; Rochette et al., 2004). Since manure type and application method are likely to affect fluxes in the longer term, comparisons after only 24 or 72 hrs will not represent the full impact of the manure or application treatment. Similarly, measurements made several weeks or months after application may miss important short-term pulses of GHG.

4.5.2 Effect of Application Rate on GHG Emissions

Generally, absolute fluxes of N_2O and CO_2 increased with application rate, although only the CO_2 fluxes from the manured plots were distinguishable from the control plots.

Although it is not apparent based on the Figure 4.3c, which shows the effect of application rate on mean N_2O fluxes, the statistical test used the median values which were highly variable and resulted in no significant difference among application rates (including 0X). Even though the critical P value was set to a conservative 0.05 in this study, the P values for the effect of application rate on N_2O flux at each of the locations were high (0.585, 0.447, 0.477). However, the manure did significantly contribute to CO_2 and CO_2-e fluxes as those values were significantly affected by manure application. Therefore, it appears that manure addition increased microbial populations and activity (and thus, CO_2 by respiration), but the onset of N transformations such as nitrification and denitrification may not have yet been sufficient to produce significant, measurable increases in N_2O flux with the different rates. The amount of manure applied (1X, 2X or 3X) did not affect CO_2 or CO_2-e flux in the short-term.

In line with findings of the current study, Hansen et al. (1993) also found no effect of manure application rate on N_2O flux. However, the authors noted that increasing levels of cattle slurry resulted in a reduction in N_2O flux per kg NH_4-N applied (Hansen et al., 1993). Gregorich et al. (1998) also found a non-proportional CO_2 flux response with increasing application rate suggesting that proportionately more manure C was retained in the soil with increasing levels of manure applied. This effect could be due to the fact that the microbial population has a finite capacity for respiration and activity. When the GHG fluxes from this study were expressed on a per kg N applied basis (i.e.: specific flux), CO_2-e fluxes decreased (but not significantly) with application rate (Figure 4.5c). In Chapter 3, the decrease in specific odour flux with application rate was explained by the manure "piling" at higher application rates, reducing the contact area between the manure and the air. This does not seem to be a factor for the specific GHG fluxes, probably due to the increased time between application and gas flux measurement which allowed the microbes better access to particle surfaces. These results suggest that GHG emissions from manure application may be proportional to the amount of N applied, at least over the range of rates examined. These results agree with the IPCC assumption that N losses increase proportionally with the amount of N applied (IPCC, 1997; Penman et al., 2000).

The analysis of interactions (Figure I.2 in Appendix I) showed that the absolute N_2O and CO_2-e fluxes increased with application rate much faster for liquid and injected manures, suggesting that the effect of application rate may depend on manure type and application method. However, when the interactions of the specific N_2O and CO_2-e fluxes were plotted, there was no interaction between manure type or application method with application rate.

4.5.3 Effect of Soil Properties on GHG Fluxes

The WFPS of the soil in this study never exceeded 60%, so the observation by Bateman and Baggs (2005) that denitrification and N_2O production peaks between 60 and 70% WFPS could not be confirmed. However, an increase in N_2O flux was observed from the control plots at an oven dry basis moisture content of 25% compared to higher moisture contents (up to 55%, Figure 4.2a). For those soils, this corresponds to a WFPS of approximately 55%. It is possible that denitrification had already begun at this WFPS level in anaerobic microsites. There is increasing evidence that aerobic denitrification may be significant in environments where oxygen is not limiting or partially limiting because many bacteria are capable of nitrate respiration in the presence of oxygen (Bateman and Baggs, 2005).

Some researchers have suggested that application of liquids at high rates may increase the WFPS of the topsoil long enough to promote N_2O emissions by denitrification. For a typical soil with dry bulk density of 1.1 g/cm^3, a 3X application rate (112 m^3/ha or 12,000 gal/acre) can raise the WFPS by approximately 25% initially. This means that if a soil is originally at 38% WFPS (20% wet basis moisture content), a 3X application of liquid manure will temporarily raise the WFPS to 63% where denitrification is more likely to occur. The length of time the WFPS remains above 60% depends on the soil drainage, the depth of the topsoil, and evapotranspiration, among other factors. It is unclear how long the WFPS must remain above 60% to promote denitrification, but it is unlikely that the high rate application of liquid manure will cause an increase in WFPS long enough to make a large difference. Fischer and Whalen (2005) noted increased emissions within a

day of increased WFPS and it took a few days to restore aerobic conditions, likely via drainage. The 1X application of water had no effect on GHG fluxes in this study, mainly because it did not raise the WFPS above 50%.

There was no obvious explanation for the higher background N_2O flux from the Saskatoon Area site based on the soil property analysis shown in Table 4.7. The soil texture, nitrogen, carbon and organic matter contents were all considered intermediate compared to the U of S Feedlot and Humboldt Area sites. However, the fertilizer and manure application history of the Saskatoon Area site was unclear and it is possible that the Saskatoon Area site received swine manure at some point in the past, unlike the other two sites.

4.5.4 Effect of Long Term Manure Application on GHG Fluxes

It is possible that repeated applications of manure, particularly solid manure, may result in higher emissions than single applications of manure made to a field for the first time. Chang et al. (1998) monitored N_2O emissions after repeated (21 annual applications) applications of solid feedlot manure at 3 rates. The emission rates from the long term experiment were similar to long-term N-fertilizer or combining N-fertilizer and manure application, but they were higher than short-term studies with similar manure. This reflects the accumulation of NO_3 and organic matter from repeated manuring and suggests that N_2O emissions from long-term manured soils may be underestimated by quantifying fluxes from short-term manuring sites (from literature). The release of inorganic N through mineralization with time also contributed to the higher N losses from the long term sites (Chang et al., 1998). Earlier studies demonstrated that long-term application of feedlot manure resulted in the accumulation of both organic C and NO_3 in the soil profile (Sommerfeldt et al., 1988; Chang and Janzen, 1996 in: Chang et al., 1998). In contrast, results from this study showed that fluxes from the long term site at Dixon were actually lower than from the short term sites (although the complete N application history of the short term sites is uncertain). However, repeated applications of swine manure may have been the reason for increased background fluxes from the Saskatoon Area plots.

4.5.5 Contribution of CO_2, CH_4 and N_2O to overall GHG Emissions

Compared to CO_2 and N_2O fluxes, CH_4 fluxes were negligible when examining the GHG's after manure application. For liquid manure applications, N_2O emissions contributed to a slightly higher proportion of the total emission than for solid manure applications. This difference was probably due to the high availability of ammonium in liquid form (Mooleki et al., 2002). The N_2O emissions contributed to a significantly higher proportion of the total emission in the injected applications compared to the surface treatments, probably due to the anaerobic conditions under the soil surface promoting denitrification.

Although more than 80% of the total CO_2-e emissions from manure applied plots comes from CO_2 (Figure 4.8), N_2O fluxes appear to be more sensitive to management practices and environmental conditions. CO_2 production is the result of oxidation of soil C by heterotrophs, which is driven by the availability of substrates (Rochette and Gregorich, 1998 in: Rochette et al. 2000a). Therefore, CO_2 fluxes are a result of microbial respiration and are less easily controlled whereas N_2O can be managed by limiting unused N in the soil profile (matching application rates to crop requirements) and by discouraging conditions for denitrification such as by managing placement.

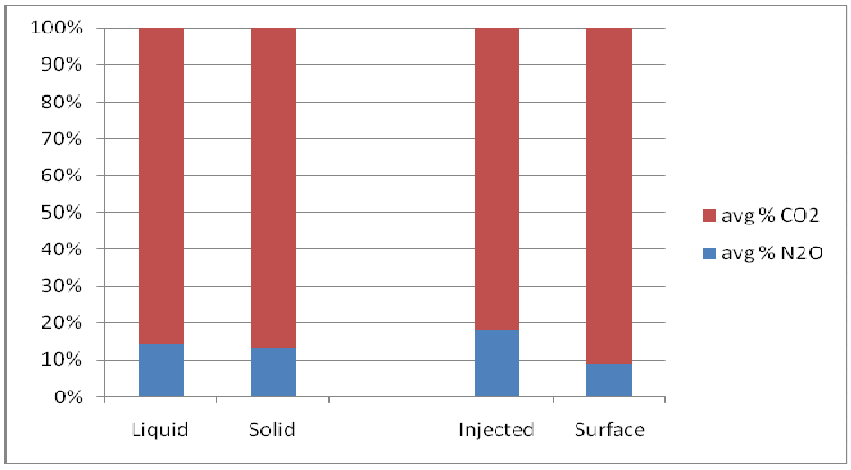


Figure 4.8. Contribution of CO_2 and CO_2 equivalent N_2O to overall CO_2-e flux from manure applied plots (2007 data only). This information is summarized in Table 4.12 for each location.

4.6 Summary and Conclusions

The GHG fluxes from solid and liquid manure using both surface and sub-surface application methods were measured using static chambers and gas chromatography. Results are presented as absolute flux for all gases (CO_2, CH_4, N_2O), specific flux (gas flux per kg N applied) for all gases, and manure induced flux (background or control flux subtracted from the absolute or actual flux) for N_2O. The results of the absolute flux analysis showed that injection significantly increased CO_2-e fluxes for both solid and liquid manure. The overall CO_2-e fluxes from the injected treatments were 3.2 times higher than CO_2-e fluxes from the surface applied plots, mainly due to a pronounced increase in N_2O fluxes. This is explained by creating conditions with liquid injection that are highly conducive to the conversion of the available N and C to GHG, especially N to N_2O and N_2 by denitrification.

The CO_2-e fluxes from the liquid manure applications were also higher than the CO_2-e fluxes from the solid manure applications. This was likely due to a high proportion of N in liquid manure in the ammonium form due to the anaerobic conditions during liquid manure storage (Schoenau and Davis, 2006). The solid manures used in this study had very little ammonium available for nitrification and denitrification. However, this comparison was made only 24 hrs after application. Solid manure generally has a higher C content, which will mineralize over time, likely providing for sustained denitrification if the conditions remain anaerobic. It is likely that conditions beneath the soil surface will remain anaerobic for long periods of time as the diffusion rate of oxygen into the topsoil is often lower than the rate of oxygen use by the increased microbial activity.

The CH_4 fluxes were generally low and the treatments had no effect in this study. Solid manure applications tended to have lower CH_4 fluxes than liquid manure and injected plots tended to have lower CH_4 fluxes than surface applied plots. Overall, the CH_4 emissions from manure application are typically short lived and insignificant compared to CH_4 emissions from enteric fermentation.

Doubling and tripling a one year agronomic application rate had no significant effect on the CO_2-e fluxes, although the absolute flux tended to increase with increased application rate. However, the specific flux (the flux per kg N applied) remained relatively constant with application rate. This indicates that GHG emissions from manure applications were approximately proportional to the amount of manure applied in this study.

When deciding whether or not to inject manure, producers must evaluate the overall environmental and economic impact of the technology. On one hand, subsurface application of livestock manure often constitutes an effective means to reduce odour emissions (refer to Chapter 3). However, the need to limit odour complaints must be weighed against the potential economic and environmental costs associated with increased GHG emissions. Since it appears that subsurface application of both solid and liquid manure will increase total GHG emissions over a period of time after application, it may not be possible to reduce both odour and GHG emissions using that particular management practice. In addition, other environmental and economic issues related to subsurface manure application, such as increased soil compaction, increased energy requirements, soil disturbance, and the increased field area required to dispose of the manure at agronomic rates, must also be considered when assessing the overall impacts of manure injection compared to surface application.

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Appendix E—Literature Values for GHG Fluxes from Manure Application

Table E.1. Summary of literature values for N_2O emissions from manure application.

Reference	Method	Emission/ Flux	Units (as reported)	Flux (ng N_2O-N/m^2-s)	Treatments	Other information
Akiyama and Tsuruta (2003)	static chamber	400 max 200 max 100 max	µg N_2O-N/m^2-hr	111 max 55.6 max 27.8 max	poultry dried swine manure compost urea	Equal amt N applied (15 g N/m^2), peaked within 2 weeks of application (app), back to background within 1 month.
Amon et al. (2005)	static chamber	24.0 28.6 31.2 52.5 54.2	g N_2O/m^3 slurry	35.35 avg 42.13 avg 45.96 avg 77.34 avg 79.84 avg	untreated separated digested straw cover aerated	All slurries applied to grassland at 40 m^3/ha. Fluxes represent total emission over 20 days after application, applied over 27 m^2.
Barton and Schipper (2001)	static chamber	25 max 7 max 16 max 22 max 2 max	g N_2O-N/ha-hr	694.4 max 194.4 max 444.4 max 611.1 max 55.6 max	dairy farm effluent, peat soil, spring app dairy farm effluent, mineral soil, spring app dairy farm effluent, peat soil, autumn app dairy farm effluent, mineral soil, autumn app control soils	All peaks within 24 hrs of app at a rate of 50 kg N/ha.
Chadwick et al. (2000)	automated flow through chambers	1.51 0.77 0.30 0.34 0.57 0.21	kg N_20-N/ha	72.82 avg 37.13 avg 14.47 avg 16.40 avg 27.49 avg 10.13 avg	dairy slurry pig slurry control dairy slurry pig slurry control	Equal NH_4-N rates, 50, 18, 0 m^3/ha, respectively. Equal volumetric rates, 30 m^3/ha. Fluxes monitored for 24 days
Chadwick et al. (2000)	static chamber	0.74 0.15 0.19 0.65 0.22 0.02	kg N_2O-N/ha	35.68 avg 7.23 avg 9.16 avg 31.34 avg 10.61 avg 0.965 avg	pig slurry dairy slurry pig FYM beef FYM layer manure control	50 m^3/ha for slurry, 50 Mg/ha for solid. Fluxes monitored for 24 days.
Chang et al. (1998)	static chamber	1.0 max 0.2 avg 56 23 11 0.7	kg N_2O-N/ha-day kg N_2O-N/ha	1157 max 231.5 avg 177.6 avg 72.93 avg 34.88 avg 2.22 avg	solid feedlot manure 180 Mg/ha 120 Mg/ha 60 Mg/ha 0 Mg/ha	Soil receiving 180 Mg/ha-yr of solid feedlot manure for 21 years. Cumulative losses monitored over 1 year.
Comfort et al. (1990)	lab set up	125 max	g N_2O-N/ha-day	144.68 max	Simulated dairy manure injection	Peak flux occurred within 2 days of app of 79,000 L/ha
Dendooven et al. (1998)	lab set up	28 28 24	g N_2O-N/ha-day	32.41 avg 32.41 avg 27.78 avg	injected pig slurry surface applied pig slurry control	
Flessa and Beese (2000)	lab set up	1.8 26.2 328.2	mg N_2O-N/m^2	0.331 avg 4.81 avg 60.29 avg	control surface application slit injection	9 week cumulative, 43.6 m^3 cattle slurry/ha

Table E.1. Summary of literature values for N_2O emissions from manure application (con't)

Ginting et al. (2003)	static chamber	5 avg 30 max	g N_2O-N/ha-day	5.79 avg 34.72 max	manured soil manured soil	4 years after manure application stopped
Goodroad et al. (1984)	static chambers	166 max 111 max	ng N_2O-N/m^2-s	166 max 111 max	manured soil (spring thaw peak) manured soil (shortly after app)	33 Mg/ha of manure applied annually for 3 years. Fluxes monitored for 1 full year
Gregoritch et al. (2005)	literature values	2.83 avg 0.99 avg	kg N_2O-N/ha-year	8.97 avg 3.14 avg	liquid manure solid manure	Average of reported values, typically monitored for 1 year after application
Hansen et al. (1993)	static chamber	80 max 50 max 60 max 40 max 5 max	mg N_2O-N/m^2-day	925.9 max 578.7 max 694.4 max 462.9 max 57.9 max	140 kg N/ha NPK, uncompacted soil 189 kg N/ha cattle slurry, uncompacted soil 140 kg N/ha NPK, compacted soil 81 kg N/ha cattle slurry, compacted soil unfertilized compact and uncompacted soil	
Jarecki et al. (2008)	lab set up	63 max 55 max 10 max	mg N_2O-N/m^2-day	729.2 max 636.6 max 115.7 max	swine manure slurry UAN control	Fluxes were monitored for 8 weeks, returned to background within 40 days. Rate was 200 kg N/ha)
Lessard et al. (1996)	static chamber	0.07 max 0.171 max 0.494 max	mg N_2O/m^2-hr	12.37 max 30.22 max 87.32 max	control 170 kg N/ha solid dairy manure (56 Mg/ha) 339 kg N/ha solid dairy manure (112 Mg/ha)	Peak fluxes occurred within 50 days of app, returned to background within 150 days of app.
Lovanh et al. (2008)	static chamber	0.20 avg 0.22 avg 0.89 avg 0.24 avg	mg N_2O/m^2-hr	35.35 avg 38.89 avg 157.32 avg 42.42 avg	control row injection surface application aerway injection	All fluxes measured 1 day after application of 200 kg N/ha of swine manure
Meng et al. (2005)	static chamber	150 avg 856 avg	g N_2O-N/ha-year	0.476 avg 2.71 avg	background 300 kg N/ha of organic manure	Organic manure = wheat straw, oil cake and cotton cake
Paul et al. (1993)	lab set up	15 max 10 max	µg N/kg soil-hr		liquid dairy manure at 100 g/kg soil solid beef manure at 100 g/kg soil	
Perala et al. (2006)	static chamber	660 400 1100 290	g N_2O-N/ha	5.09 avg 3.08 avg 8.49 avg 2.24 avg	slurry injection and mineral fertilizer slurry incorporation and mineral fertilizer slurry injection mineral fertilizer	79 kg N/ha and 50 kg N/ha 79 kg N/ha and 50 kg N/ha 157 kg N/ha 100 kg N/ha Fluxes monitored over approximately 5 months during summer
Peterson (1999)	static chambers	10 max 25 max 10 max 15 max 13 max	g N_2O-N/ha-day	11.57 max 28.94 max 11.57 max 17.36 max 15.04 max	digested slurry at seeding untreated slurry at seeding fertilizer at seeding digested slurry at 5 weeks untreated slurry at 5 weeks	All treatments had rates of 100 kg NH_4-N/ha, fluxes were monitored over 100 days.
Rochette et al. (2000b)	static chamber	425 max 0.62 1.23 1.65	ng N_2O-N/m^2-s % of total N applied emitted as N_2O	425 max	pig slurry application control 60 Mg/ha 120 Mg/ha	Peak fluxes were limited to about 30 days (warm soil conditions), and began within 1 month of application of 60 and 120 Mg/ha.

Table E.1. Summary of literature values for N_2O emissions from manure application (con't)

Rochette et al. (2004)	static chamber	1.5 max 3.5 max 599 323 174	mg N_2O/m^2-hr mg N_2O-N/m^2	265.15 max 618.69 max	fall applied pig slurry spring applied pig slurry cumulative N loss for spring applied slurry cumulative N loss for fall applied slurry cumulative N loss for NH_4NO_3 control	Peak fluxes in fall occurred within days of application of 200 kg N/ha, peak fluxes in spring occurred within weeks of application. Cumulative losses monitored for 1 year.
Scott et al. (1999)	static chamber	2500-3500 max	µg N_2O-N/m^2-hr	694.4-972.2 max	sewage sludge incorporation at 185 Mg/ha.	Peaks occurred within 46 days of application and corresponded with rainfall.
Sharpe and Harper (1997)	micromet	0.019 avg 250-380 avg 4.7	g N_2O-N/ha-day kg N_2O-N/ha	0.02199 avg 289.4-439.8 avg	background after sprinkler irrigation of swine effluent cumulative loss over 100 days	Total of 70 mm swine effluent applied over 12 ha.
Sherlock et al. (2002)	static chamber	0.08 avg 1.0 avg 7.5-15.8 max	g N_2O-N/ha-hr	2.22 avg 27.77 avg 208.3-438.9 max	control for 14 days after pig slurry application (60 m^3/ha) peaks	Peaks occurred approx 60 days after app, coincided with rainfall events, fluxes monitored for 80 days.
Van Groenigen et al. (2004)	static chamber	120 (max) 10 (max) 30 (max) 180 (max) 120 (max) 180 (max)	g N_2O-N/ha-day	138.9 max 11.57 max 34.72 max 208.33 max 138.89 max 208.33 max	cattle slurry on sandy soil fertilizer on sandy soil cattle slurry + fertilizer on sandy soil cattle slurry on clay soil fertilizer on clay soil cattle slurry + fertilizer on clay soil	All treatments had a 200 kg N/ha application rate. Fluxes monitored over 180 days, peaks occurred within 30 days on sandy soil, but some peaks occurred at day 150 for clay soil
Wagner-Riddle and Thurtell (1998)	micromet	0 – 4.8 370 max 614 max	kg N/ha ng N_2O/m^2-s	 235.4 max 390.7 max	manure, fertilizer, alfalfa, fallowing bare soil following spring thaw and manure application	cumulative N loss from Jan to April (this period is usually ignored and assumed to have zero flux)
Wagner-Riddle et al. (1997)	Micromet	5.7 – 7.4 avg <0.2 3.23	kg N_2O-N/ha-year kg N_2O-N/ha-month	18.07-23.47 avg <7.71 avg 124.5 avg	Manure + fallow typical during "emission periods"	
Watanabe et al. (1997)	static chamber	1 max 0.4 max 0.2 max 0.1 max	mg N_2O-N/m^2-hr	277 max 111.11 max 55.56 max 27.78 max	swine slurry, fall app cattle slurry, fall app swine slurry, winter app cattle slurry, winter app	Rates not stated, but were same for fall and winter experiments. Peak fluxes occurred within weeks of app in fall experiment, but took several months to peak in winter experiment.

Table E.1. Summary of literature values for N_2O emissions from manure application (con't)

Weslien et al. (1998)	static chambers and FTIR mega-chambers	48 max 52 max 150 max 125 max 80 max	µg N_2O-N/m^2-hr	13.33 max 14.44 max 41.67 max 34.72 max 22.22 max	control trenching shallow injection band spreading + harrowing band spreading	Pig slurry applied at 83-96 kg NH_4-N/ha. Fluxes monitored for 40 days. Most peaks occurred within 4 days of app.
		0.24 0.51 0.59 0.65 0.54	kg N_2O-N/ha	6.94 avg 14.76 avg 17.07 avg 18.81 avg 15.62 avg	control trenching shallow injection band spreading + harrowing band spreading	Spring application, cumulative emissions over 40 days.
		0.45 1.21 1.40 1.24		13.02 avg 35.01 avg 40.51 avg 35.87 avg	control trenching band spreading + harrowing band spreading	Fall application, cumulative emissions over 40 days.
Wulf et al. (2002b)	static chamber	125 max 175 max 10 max 25 max 100 max 10 max	µg N_2O-N/m^2-hr	34.72 max 48.61 max 2.78 max 6.94 max 27.78 max 2.778 max	splash plate on grassland injection on greassland grassland control splash plat on arable land injection on arable land arable land control	Slurry applied at 114 kg N/ha. Fluxes monitored for 6 weeks.
		210 100 75 75 350 100 90 80	g N_2O-N/ha	5.79 avg 2.76 avg 2.07 avg 2.07 avg 9.65 avg 2.76 avg 2.48 avg 2.20 avg	injected digested slurry on arable land harrowed digested slurry on arable land splash plate digested slurry on arable land trail hose digested slurry on arable land injected digested slurry on grassland splash plate digested slurry on grassland trail hose digested slurry on grassland trail shoe digested slurry on grassland	Cumulative emissions over 6 weeks.
This study	static chamber	0.0305 avg 0.3440 avg 0.0337 avg 0.0217 avg 0.2950 avg	µg N_2O/m^2-s	19.41 avg 218.9 avg 21.44 avg 13.81 avg 187.73 avg	control (bare soil) liquid manure solid manure surface application sub-surface application	Average values measured 24 hrs after application for a range of application rates (0 to 500 kg N/ha) .

Table E.2. Summary of literature values for CH_4 emissions from manure application.

Reference	Method	Emission/ Flux	Units (as reported)	Flux (ng CH_4-C/m^2-s)	Treatments	Other information
Amon et al. (2005)	static chamber	1.3 19.7 2.0 22.2 7.6	g CH_4 per m^3 slurry	4.01 avg 60.8 avg 6.17 avg 68.5 avg 23.46 avg	untreated separated digested straw cover aerated	All slurries applied to grassland at 40 m^3/ha. Fluxes represent total emission over 20 days after application.
Chadwick and Pain (1997)	static chamber, in lab	2.4 max 0.8 max 0.1 max 1.5 max 1.0 max	mg CH_4-C/m^2-hr	666.67 max 222.2 max 27.78 max 416.7 max 277.8 max	pig slurry on clay soil pig slurry on sandy soil no slurry, average of both soils dairy slurry on clay soil dairy slurry on sandy soil	All max fluxes were immediate, returned to background within 48 hrs after app of 25 m^3/hr.
Chadwick et al. (2000)	automated flow through chambers	580 133 -33 -7.41 -2.10 -11.01	g CH_4/ha	37.29 avg 8.55 avg -2.12 avg -0.476 avg -0.135 avg -0.708 avg	dairy slurry pig slurry control dairy slurry pig slurry control	Equal NH_4-N rates, 50, 18, 0 m^3/ha, respectively. Cumulative losses over 24 days. Equal volumetric rates, 50 m^3/ha. Cumulative losses over 24 days.
Chadwick et al. (2000)	static chamber	0.40 0.24 2.29 0.04 -0.07 -0.10	g CH_4/ha	0.0257 avg 0.0154 avg 0.147 avg 0.00257 avg -0.0045 avg -0.00643 avg	pig slurry dairy slurry pig FYM beef FYM layer manure control	50 m^3/ha for slurry, 50 Mg/ha for solid. Cumulative losses over 24 days.
Flessa and Beese (2000)	lab set up	5.0 3.4 0.1	mg CH_4-C/m^2	0.919 avg 0.625 avg 0.0184 avg	control surface application slit injection	43.6 m^3 cattle slurry/ha, cumulative loss over 9 weeks.
Ginting et al. (2003)	static chamber	5 avg 15 max	g CH_4-C/ha-day	5.79 avg 17.36 max	manured soil	4 years after application stopped
Jarecki et al. (2008)	lab set up	16 max 4 max 0 max	mg CH_4-C/m^2-day	185.2 max 46.3 max 0 max	swine manure slurry UAN control	Fluxes were monitored for 8 weeks, returned to background within 20 days of app of 200 kg N/ha
Lessard et al. (1997)	static chamber	-0.012 to 0.004	mg CH_4/m^2-hr	-4.44 to 1.48	manured soil	Stockpiled dairy manure at 0, 56, 112 Mg/ha and composted dairy manure at 100 Mg/ha.
Lovanh et al. (2008)	static chamber	0 avg -0.14 avg 8.75 avg 2.27 avg -2.86 -0.97 0.22 1.51	mg CH_4/m^2-hr	0 avg -51.85 avg 3240.7 avg 840.7 avg -1059.3 avg -359.3 avg 81.48 avg 559.3 avg	control row injection surface application airway injection control row injection surface application airway injection	All fluxes measured 24 hrs after application of 200 kg N/ha of swine manure. All fluxes measured 72 hrs after application of 200 kg N/ha of swine manure.

Table E.2. Summary of literature values for CH_4 emissions from manure application (con't).

Perala et al. (2006)	static chamber	-150 50 -290 -14	g CH_4-C/ha	-1.16 avg 0.386 avg -2.24 avg -0.108 avg	slurry injection and mineral fertilizer slurry incorporation and mineral fertilizer slurry injection mineral fertilizer	79 kg N/ha and 50 kg N/ha 79 kg N/ha and 50 kg N/ha 157 kg N/ha 100 kg N/ha Cumulative fluxes monitored over approximately 5 months during summer.
Sherlock et al. (2002)	static chamber	39.33 max 10.0 max	g CH_4-C/ha-hr	1092.5 max 277.8 max	immediately after swine slurry app within 6 hours of application	App rate: 60 m^3/ha
Wulf et al. (2002b)	static chamber	1.25 max 1.0 max 1.0 max 3.2 max 150 35 20 300 110 1	mg CH_4-C/m^2-hr g CH_4-C/ha	347.2 max 277.8 max 277.8 max 888.9 max 4.13 avg 0.965 avg 0.551 avg 8.27 avg 3.03 avg 0.028 avg	harrowed on arable land trail hose on arable land splash plate on arable land trail hose on grassland untreated slurry on arable land digested slurry on arable land control arable land untreated slurry on grassland digested slurry on grassland control grassland	Slurry applied at 114 kg N/ha. Fluxes monitored for 6 weeks. Cumulative losses from trail hose application over 6 weeks.
This study	static chamber	0.039 avg 0.049 avg -0.010 avg 0.020 avg 0.012 avg	µg CH_4/m^2-s	52.0 avg 65.33 avg -13.33 avg 26.67 avg 16.0 avg	control (bare soil) liquid manure solid manure surface application sub-surface application	Average values measured 24 hrs after application for a range of application rates (0 to 500 kg N/ha)

Table E.3. Summary of literature values for CO_2 emissions from manure application.

Reference	Method	Emission/ Flux	Units (as reported)	Flux ($\mu g\ CO_2\text{-}C/m^2\text{-}s$)	Treatments	Other information
Barton and Schipper (2001)	closed chamber	3000 max 3000 max 3200 max 4500 max 2000 max	g CO_2-C/ha-hr	83.33 max 83.33 max 88.88 max 125 max 55.56 max	dairy farm effluent, peat soil, spring app dairy farm effluent, mineral soil, spring app dairy farm effluent, peat soil, autumn app dairy farm effluent, mineral soil, autumn app control soils	All peaks occurred within 24 hrs of application of 50 kg N/ha
Dendooven et al. (1998)	lab set up	5.66 avg 5.65 avg 1.16 avg	kg CO_2-C/ha-day	6.55 avg 6.53 avg 1.34 avg	injected pig slurry surface applied pig slurry control	
Flessa and Beese (2000)	lab set up	29.1 50.8 51.2	g CO_2-C/m^2	5.34 avg 9.33 avg 9.41 avg	control surface application slit injection	43.6 m^3 cattle slurry/ha, cumulative losses over 9 weeks.
Ginting et al. (2003)	static chamber	4.4 5.1 50	mg CO_2-C/ha-yr kg/ha-day		control synthetic N 100 days after app	
Gregorich et al. (1998)	static chamber	90 max 60 max 40 max	kg CO_2-C/ha-day	104.2 max 69.4 max 46.30 max	112 Mg/ha 56 Mg/ha 0 Mg/ha	Solid manure and straw litter, incorporated
Jarecki et al. (2008)	lab set up	5 max 2 max 2 max	g CO_2-C/m^2-day	57.87 max 23.15 max 23.15 max	swine manure slurry UAN control	Fluxes were monitored for 8 weeks, returned to background within 25 days of application of 200 kg N/ha
Lovanh et al. (2008)	static chamber	212 avg 151 avg 1231 avg 399 avg	mg CO_2/m^2-hr	215.9 avg 153.8 avg 1253.8 avg 406.4 avg	control row injection surface application aerway injection	All fluxes measured 1 day after application of 200 kg N/ha of swine manure.
Rochette et al. (2000a)	static chamber	1.5 max 0.1 max 769 1658	mg CO_2/m^2-s kg CO_2-C/ha kg CO_2-C/ha	5500 max 366.7 max 2.44 avg 5.26 avg	pig slurry application at 60 and 120 Mg/ha control (fertilizer) 60 Mg/ha 120 Mg/ha	Peak occurred approx 1 month after application. Cumulative losses over 1 year.
Rochette et al. (2004)	static chamber	142.5 118.6 91.4	g CO_2-C/m^2	4.52 avg 3.76 avg 2.90 avg	cumulative C loss for spring applied pig slurry cumulative C loss for fall applied pig slurry cumulative C loss for NH4NO3 control	Cumulative losses over 1 year, 200 kg N/ha applied
Scott et al. (1999)	static chamber	200 avg	mg CO_2-C/m^2-hr	55.56 avg	sewage sludge incorporation	Fluxes steady for 40 days, diurnal variation, 185 Mg/ha
Watanabe et al. (1997)	static chamber	1200 max 1000 max	mg CO_2/m^2-hr	1222.2 max 1018.5 max	cattle slurry, fall app swine slurry, fall app	Peak fluxes occurred within days of app, monitord for 2 months after app.
This study	static chamber	58.0 avg 238.8 avg 65.6 avg 78.8 avg 190.5 avg	µg CO_2/m^2-s	212.7 avg 875.6 avg 240.5 avg 288.9 avg 698.5 avg	control (bare soil) liquid manure solid manure surface application sub-surface application	Average values measured 24 hrs after application for a range of application rates (0 to 500 kg N/ha)

Appendix F—Gas Chromatography Specifications

CO_2 concentration analysis utilized a Varian Micro GC CP-2003 with a Poraplot U column (10 m long, 0.32 mm inner diameter, 100ºC) with a 150 ms injection time and a 110ºC injector temperature. The CO_2 was identified using a thermal conductivity detector (TCD) with helium carrier gas. The initial and final pressures of the Micro GC were 100 kPa. The detection limit for CO_2 was 80 ppm.

N_2O and CH_4 concentration analysis utilized a Varian CP-3800 gas chromatograph with an injector temperature of 70ºC and a split ratio of five. N_2O was detected with one of 2 electron capture detectors (ECD's) with Poraplot Q coated fused silica columns (10 m long, 0.32 mm diameter, 0.32 μm film thickness). Oven and detector temperatures for the ECD's were 35 and 370ºC respectively and the front and back pressures were 12.5 and 20 psi respectively. Front and back column flows were 7.9 and 14.4 mL/min.

The detector used for CH_4 detection was a flame ionization detector (FID) with a fused silica column coated with carboplot P7 (25 m long, 0.53 mm diameter, 0.25 μm film thickness). The FID pressure was 15 psi and the column flow was 3 mL/min. The oven and detector temperatures were 35 and 200ºC respectively. The carrier gas for both detectors was helium. The detection limits for N_2O and CH_4 were 60 and 360 ppb, respectively.

Appendix G—Sample Calculations for Flux Calculation and Comparison of Calculation Methods

The following outlines the calculation of chamber volume and CO_2 and N_2O gas flux by both calculation methods (Hutchinson and Mosier and regression) for the solid swine surface applied 3X plot (rep 3).

Table G.1. Gas concentration data from solid swine surface 3X-3 plot.

Time (min)	N_2O concentration (ppm)	CO_2 concentration (ppm)
0	0.29905	383.196
5	0.47018	579.087
10	0.60096	707.5627
15	0.69571	753.4675

Depths measured through open port: 0.13, 0.14, 0.175, 0.195 m (average = 0.16 m).

The volume of the chamber was calculated from this average depth using Equation G.1.

$$V = height * area - v \quad \text{(G.1)}$$

Where V = chamber volume (m^3),

Height = average internal height of chamber (average depth – 0.03 m where 0.03 m is the height of the open port above the top of the inside of the chamber) ,

Area = average cross sectional area of chamber (0.2826 m^2), and

v = average volume of internal components (0.00038015 m^3) as measured by water displacement before construction.

For this plot, V = (0.16-0.03)*0.2826-0.00038015 = 0.03636 m^3

G.1: Sample calculation for N_2O flux using Hutchinson and Mosier model

$$F = \frac{\rho V (C_1 - C_o)^2}{At(2C_1 - C_2 - C_o)} \ln \frac{C_1 - C_o}{C_2 - C_1}, if \frac{C_1 - C_o}{C_2 - C_1} > 1 \quad \text{(G.2)}$$

Where F = gas flux (mass per unit area per unit time),

ρ = density of gas (1.96 kg/m^3 for both N_2O and CO_2),

V = volume of chamber (0.03636 m^3),

A = cross sectional area of chamber (0.2826 m^2),
t = time interval (5 min),
C_o = concentration of sub-sample drawn at time = 0,
C_1 = concentration of sub-sample drawn at time = t_1, and
C_2 = concentration of sub-sample drawn at time = t_2 ($t_2 = 2t_1$ for the equation to be valid).

$$F = \frac{1.96\frac{kg}{m^3}\,0.03636 m^3 (0.47018 - 0.29905)^2}{0.2826 m^2 (5\,\text{min})(2(0.47018) - 0.60096 - 0.29905)} \ln\frac{0.47018 - 0.29905}{0.60096 - 0.47018}$$

$$F = 0.0098435\frac{mg}{m^2 - \text{min}}$$

$$F = 0.164\frac{\mu g}{m^2 - s}$$

G.2: Sample calculation for N_2O flux using regression analysis

$$F = \rho\frac{V}{A}\frac{\Delta C}{\Delta t} \qquad \text{(G.3)}$$

Where F = gas flux (mass per unit area per unit time),
ρ = gas density (1.96 kg/m^3),
V = chamber volume (0.03636 m^3),
A = chamber area (0.2826 m^2), and
ΔC/Δt = rate of change in gas concentration at t = 0 (by regression, ppm/min).

ΔC/Δt was found using regression analysis. The concentration was plotted vs time and linear and quadratic regressions were fitted. The significance of each regression was analyzed using Minitab v. 15.

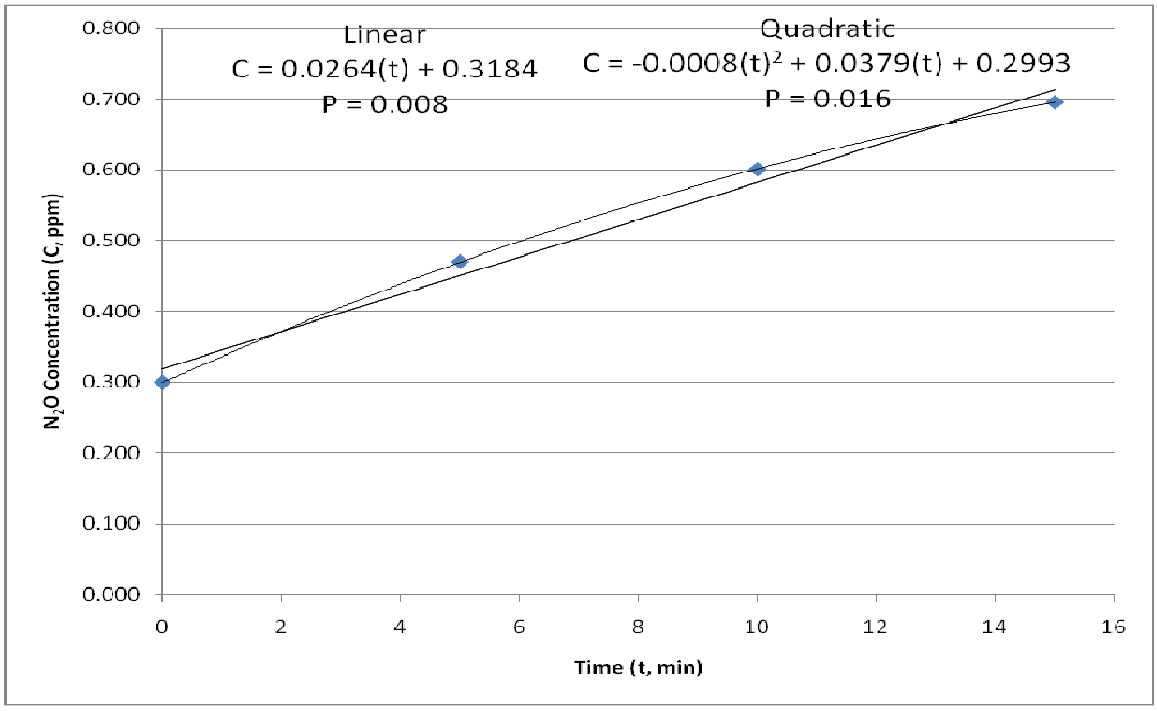


Figure G.1. Linear and quadratic regression analysis of N_2O concentration change over time for the swine solid surface 3X-3 plot.

In this case, both regressions were significant (P<0.015), indicating the first order term in the linear regression equation and the second order term in the quadratic regression equation were significant. But since the linear regression had a lower P value, it was deemed to describe the variation in concentration over time more efficiently. Therefore, the linear regression equation was differentiated with respect to time and analyzed at t = 0 to determine ΔC/Δt.

$$\frac{dC}{dt} = 0.0264$$

Therefore, dC/dt at t = 0 is 0.0264 ppm/min.

The flux (F) was

$$F = 1.96 * \frac{0.03636}{0.2826} * 0.0264$$

$$F = 0.0066575 \frac{mg}{m^2 - \min}$$

$$F = 0.111 \frac{\mu g}{m^2 - s}$$

For comparison, the flux (F) using the quadratic regression would be:

$$\frac{dC}{dt} = -0.0016(t) + 0.0379$$

Therefore, dC/dt at t = 0 is 0.0379 ppm/min.
The flux (F) would be 0.159 μg/m^2-s (30% higher than linear regression result).

G.3: Sample calculation for CO_2 flux using Hutchinson and Mosier model

The chamber area, chamber volume and gas density are the same as the N_2O flux calculation. The CO_2 concentrations over time are shown in Table G.1.

$$F = \frac{1.96\frac{kg}{m^3}\,0.03636m^3\,(579.087 - 383.196)^2}{0.2826m^2\,(5\,\text{min})(2(579.087) - 707.5627 - 383.196)} \ln\frac{579.087 - 383.196}{707.5627 - 579.087}$$

$$F = 12.1097\frac{mg}{m^2 - \text{min}}$$

$$F = 201.83\frac{\mu g}{m^2 - s}$$

G.4: Sample calculation for CO_2 flux using regression analysis

Again, regression analysis was used to determine ΔC/Δt.

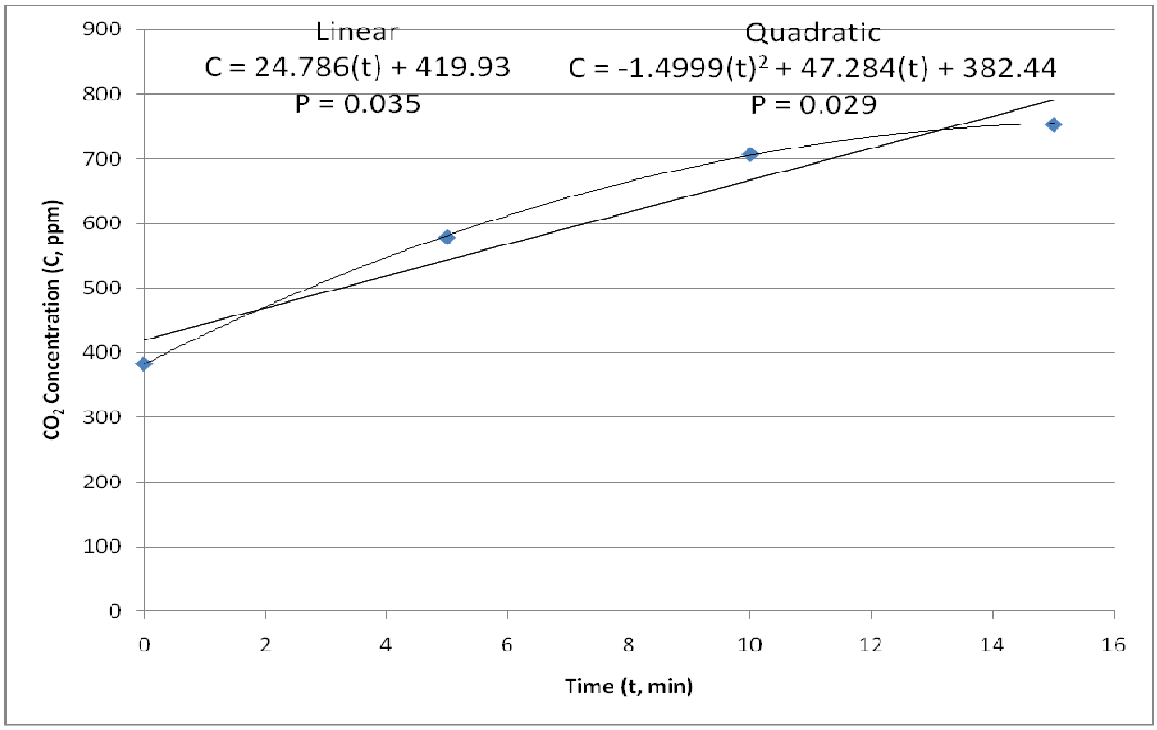


Figure G.2. Linear and quadratic regression analysis of CO_2 concentration change over time for the swine solid surface 3X-3 plot.

Again, both regressions were significant (P<0.015), but this time, since the quadratic regression had a lower P value, it was deemed to describe the variation in concentration over time more efficiently. Therefore, the quadratic regression equation was differentiated with respect to time and analyzed at t = 0 to determine $\Delta C/\Delta t$.

$$\frac{dC}{dt} = -2.999(t) + 47.284$$

Therefore, dC/dt at t = 0 is 47.284 ppm/min. The flux works out to be 198.73 µg/m^2-s. By comparison, if the linear regression value of dC/dt at t = 0 is used (24.786 ppm/min), the flux becomes 104.17 µg/m^2-s.

G.5: Discussion and comparison of calculation methods

A summary of results for the fluxes for the sample plot are shown in Table G.2. Both the linear and quadratic regressions are shown for comparison, but, for the final analysis in this case, the linear model was used for the N_2O flux and the quadratic model was used for the CO_2 flux.

Table G.2. Summary of N_2O and CO_2 flux results for solid swine surface 3X-2 plot.

Method	N_2O flux ($\mu g/m^2$-s)	CO_2 flux ($\mu g/m^2$-s)
Hutchinson and Mosier	0.164	201.83
Linear regression	0.111	104.17
Quadratic regression	0.159	198.73

The Hutchinson and Mosier model was considered valid if the natural log term in the model was greater than 1. Using this criteria, the model was valid for 86 of the 123 N_2O fluxes (70%), and it was valid for 86 of the 123 CO_2 fluxes (70%). However, if the model was valid for the N_2O flux from a plot, it was not necessarily valid for the CO_2 from that plot, and vice versa. It was noted that the Hutchinson and Mosier model tended to be invalid when the flux was low (i.e.: from the solid feedlot surface plots) for both gases.

In most cases where the Hutchinson and Mosier model was valid (the natural log term was greater than zero), the quadratic regression was significant. The flux calculated using the quadratic regression was always higher than the flux calculated using the linear regression (as was the case in Lovanh et al., 2008) and was usually very close to the flux calculated using the Hutchinson and Mosier model (refer to Table C.2). This was not unexpected since the Hutchinson and Mosier model is a curvilinear relationship to account for the suppression of emissions due to decreased concentration gradient. However, the Hutchinson and Mosier model only accounts for the first three data points whereas the quadratic regression accounts for all four data points. Also, there was no way to determine if the Hutchinson and Mosier model was statistically significant (the flux is significantly different from zero) whereas there was a statistical test for the regression models.

Due to their lower P values during the regression analysis, linear regression models were used in the majority of cases. A summary of the number of times linear regression was used vs. quadratic regression is shown in Table G.3.

Table G.3. Summary of regression frequencies. Both gases had a total of 123 fluxes.

Gas	Number of linear regressions used	Number of quadratic regressions used	Number of insignificant regressions
N_2O	83	12	28
CO_2	94	13	16

Note: the quadratic regression was significant but not used (because linear regression had a lower P value) 10 times for N_2O and 17 times for CO_2 flux analysis. A breakdown of which treatments these occurred in appears in Tables I.6 and I.8 in Appendix I.

A comparison of fluxes and P values for the main treatments calculated using the Hutchinson and Mosier model and regression models appears in Tables G.4 and G.5. In

Table G.4, when the Hutchinson and Mosier model was not valid, a modified linear regression described in Ginting et al. (2003) was used to calculate the flux using Equation G.3. For Table G.5, the regression (linear or quadratic) with the lower P value was used. If the P value for both regressions was greater than 0.15, the flux was technically not significantly different from zero and was assumed to be zero.

Table G.4. Summary of fluxes and P values as calculated using the Hutchinson and Mosier model. All fluxes have units of µg/m^2-s.

Treatment	N	Mean N_2O flux	P value	Mean CO_2 flux	P value	Mean CO_2-e flux	P value
Liquid	51	0.493	0.101	436.8	0.000	589.6	0.000
Solid	72	0.082		144.6		170.0	
Injected	63	0.422	0.000	300.0	0.035	430.9	0.026
Surface	60	0.074		229.8		252.7	
0X	33	0.052	0.245	104.2	0.000	120.3	0.001
1X	30	0.249		208.9		286.1	
2X	30	0.331		334.5		437.0	
3X	30	0.397		431.5		555.0	

Table G.5. Summary of fluxes and P values as calculated using linear or quadratic regression. All fluxes have units of µg/m^2-s.

Treatment	n	Mean N_2O flux	P value	Mean CO_2 flux	P value	Mean CO_2-e flux	P value
Liquid	51	0.334	0.049	252.2	0.000	242.7	0.000
Solid	72	0.055		71.81		74.97	
Injected	63	0.292	0.000	190.2	0.003	279.6	0.001
Surface	60	0.044		100.8		86.1	
0X	33	0.047	0.201	61.52	0.021	71.8	0.054
1X	30	0.160		122.3		163.4	
2X	30	0.196		180.9		240.2	
3X	30	0.292		230.2		299.6	

Overall, the fluxes calculated using the Hutchinson and Mosier model were 31, 45 and 49% higher for N_2O, CO_2 and CO_2-e than the regression analysis, respectively. However, the trends and treatment effects were very similar for both methods, even for a conservative critical P value of 0.05. Although the calculation method had little effect on the treatment comparisons, regression analysis is recommended for future studies of this nature. Regression analysis works well with relatively low fluxes, allows for statistical

tests to ensure the flux is significantly different from zero and allows the use of all data points collected.

Appendix H—Sensitivity Analysis of Flux Calculation

The equation used to calculate GHG flux from the static chamber was

$$F = \rho \frac{dC}{dt} \frac{V}{A} = \rho V dC A^{-1} dt^{-1} \quad \text{(H.1)}$$

Where F = GHG flux (mg/m^2-min),
ρ = density of gas (kg/m^3),
dC = change in concentration (ppm),
dt = change in time (min),
V = volume of chamber (m^3), and
A = area of chamber (m^2).

Therefore, the uncertainty in GHG emission depends on the uncertainty in:

1. Density of gas (±0.1 kg/m^3 for all three gases)
2. Gas concentration measurement (±4 ppm for CH_4, ±0.01 ppm for N_2O, ±20 ppm for CO_2)
3. Time measurement (±0.333 min)
4. Volume measurement/calculation (±0.001089 m^3)
5. Area measurement (±0.0095 m^2)

1. At 20°C, the density of methane is 0.72 kg/m^3, the density of carbon dioxide is 1.96 kg/m^3 and the density of nitrous oxide is 1.96 kg/m^3. The uncertainty of all of these densities comes from the density fluctuation due to temperature during the sampling period. This uncertainty (due to temp fluctuation of approximately 10°C) was approximately 0.1 kg/m^3.
2. The uncertainty in the gas concentration measurement comes from the gas chromatograph specifications. The uncertainty in CH_4 measurement was ±2 ppm, ±0.005 ppm for N_2O and ±10 ppm for CO_2. Because the equation uses a delta C value, the overall error in the gas concentrations was two times the uncertainty in the individual measurements.
3. The uncertainty in the time measurement was variable and depended on the skill of the user and their ability to draw samples at the designated time. From experience, the time uncertainty for any one measurement was 10 seconds (0.167 min). Again, because the equation uses delta t, the overall uncertainty was ±0.333 min.
4. The uncertainty in the volume measurement is related to the uncertainty in the depth/height, area and volume of internal components measurements (Equation C.1 in Appendix C). Instead of doing additional complex error calculations, the overall

uncertainty in volume measurement was assumed to be the standard deviation of all volume measurement/calculations done in the field (a total of 123 measurements). Therefore, the uncertainty in the volume measurement was ±0.001089 m^3).

5. The uncertainty in the area was determined knowing the tolerance of the measuring device used to measure the diameter of the chamber at 4 locations around the perimeter (0.01 m). With an average diameter of 0.60 m ±0.01 m, the uncertainty in the area calculation was ±0.0095 m^2.

To complete the uncertainty analysis, Equation H.1 was partially differentiated with respect to each of the 5 variables outlined above.

$$\frac{\partial F}{\partial \rho} = \frac{V}{A}\frac{dC}{dt} \quad \text{(H.2)} \qquad \frac{\partial F}{\partial dC} = \frac{\rho V}{Adt} \quad \text{(H.3)} \qquad \frac{\partial F}{\partial dt} = \frac{-\rho V dC}{Adt^2} \quad \text{(H.4)}$$

$$\frac{\partial F}{\partial V} = \frac{\rho dC}{Adt} \quad \text{(H.5)} \qquad \frac{\partial F}{\partial A} = \frac{-\rho V dC}{A^2 dt} \quad \text{(H.6)}$$

The partial derivatives (H.2, H.3, H.4, H.5, and H.6) were assessed using average values from the undisturbed control plot from the poultry trial (rep 2). This plot was chosen because it had significant, linear regressions for the CO_2 and N_2O fluxes. In addition, the flux from this plot was relatively low which would result in a higher error. Therefore, the errors calculated here could be considered a worst case scenario. The parameter values for this plot are summarized in Table H.1.

Table H.1. Parameter values for poultry undisturbed control plot (rep 2).

dC (CO_2)	80±20 ppm	ρ (CO_2)	1.96±0.10 kg/m^3
dC (CH_4)	-0.4±4 ppm	ρ (CH_4)	0.72±0.10 kg/m^3
dC (N_2O)	0.01926±0.0100 ppm	ρ (N_2O)	1.96±0.10 kg/m^3
dt	15.00±0.33 min	A	0.2826±0.0095 m^2
V	0.04554±0.001089 m^3		

The overall error in the flux calculation was then calculated using Equation H.7.

$$\%\ \text{error in F} = \frac{\sqrt{\left(\frac{\partial F}{\partial \rho}\partial\rho\right)^2 + \left(\frac{\partial F}{\partial dC}\partial dC\right)^2 + \left(\frac{\partial F}{\partial dt}\partial dt\right)^2 + \left(\frac{\partial F}{\partial V}\partial V\right)^2 + \left(\frac{\partial F}{\partial A}\partial A\right)^2}}{F} \text{x}100\% \quad \text{(H.7)}$$

The F value in the denominator was calculated using Equation H.1 and the typical values shown in Table H.1. This resulted in errors of 26%, >100% and 52% for CO_2, CH_4 and

N_2O, respectively. For all three gases, the largest contributor to the error was the uncertainty in the gas concentration measurement, followed by the uncertainty in the density of the gases. At higher fluxes, the error was considerably lower. For all plots, the range in uncertainties was 8-50% for CO_2, 9-55% for N_2O and >100% for CH_4.

Appendix I—Experimental Data

Table I.1. N_2O Outliers

		----------µg/m^2-s----------	
	Treatment	Flux	Critical Value
1	LDS 2X-2	0.0208	0.0169
2	LDS 3X-2	0.0474	0.0169
3	LDI 2X-3	0.076	0.0677
4	SFS 0X-2	0.0258	0.0024
5	SFS 1X-1	0.0033	0.0024
6	SFS 2X-2	0.0152	0.0024
7	SFI 0X-2	0.0973	0.0526
8	LSS 0X-3	0.5147	0.3216
9	LSS 3X-2	0.5519	0.3216
10	SSI 2X-1	0.2721	0.1937
11	SSI 2X-2	0.2049	0.1937
12	SPS 2X-3	0.0572	0.0239
13	SPS 3X-1	0.286	0.0239
14	SPI 1X-2	0.495	0.3741
15	SPI 2X-3	0.4175	0.3741

Table I.2. CO_2 Outliers

		----------µg/m^2-s----------	
	Treatment	Flux	Critical Value
1	LDS 3X-2	549.4	535.3
2	SFI 0X-2	174.3	124.8
3	LSS 3X-2	613.1	473.8
4	SSS 3X-3	199.0	138.1
5	SPS 2X-1	278.0	225.7

Table I.3. CO_2-e Outliers

		----------µg/m^2-s----------	
	Treatment	Flux	Critical Value
1	LDS 3X-2	564.1	539.2
2	SFI 0X-2	204.5	117.6
3	LSS 3X-2	784.2	517.8
4	SSS 3X-3	233.5	148.6
5	SPS 2X-1	282.9	237.9
6	SPS 3X-1	254.7	237.9
7	SPI 1X-2	421.2	409.0

Note: The three letters represent treatment (below), -X represents rate (control, 1 year, 2 year or 3 year rate), and the last number indicates repetition.

Note: For CO_2-e outliers, previous outliers were reintroduced and the critical values and CO_2-e outliers were determined independent from the N_2O and CO_2 outliers. There were no CH_4 outliers.

Table I.4. Summary of treatment codes.

LDS	Liquid dairy surface	SSS	Solid swine surface
LDI	Liquid dairy injected	SSI	Solid swine injected
SFS	Solid feedlot surface	LSS	Liquid swine surface
SFI	Solid feedlot injected	LSI	Liquid swine injected
SPS	Solid poultry surface	SPI	Solid poultry injected

Table I.5. N_2O data summary (without outliers).

Location	Type	Species	Mode	Rate	n	mean	stderr	
U of S	Solid	Feedlot	Injected	0X	2	0.0000	0.0000	1 outlier
				1X	3	0.0166	0.0118	
				2X	3	0.0020	0.0020	
				3X	3	0.0142	0.0083	
U of S	Solid	Feedlot	Surface	0X	2	0.0000	0.0000	1 outlier
				1X	2	0.0000	0.0000	1 outlier
				2X	2	0.0000	0.0000	1 outlier
				3X	3	0.0000	0.0000	
U of S	Liquid	Dairy	Injected	0X	6	0.0083	0.0022	
				1X	3	0.0116	0.0058	
				2X	2	0.0383	0.0082	1 outlier
				3X	3	0.0375	0.0113	
U of S	Liquid	Dairy	Surface	0X	3	0.0060	0.0034	
				1X	3	0.0062	0.0031	
				2X	2	0.0050	0.0050	1 outlier
				3X	2	0.0087	0.0004	1 outlier
Saskatoon Area	Solid	Swine	Injected	0X	3	0.0299	0.0092	
				1X	3	0.0594	0.0114	
				2X	1	0.0000	-	2 outliers
				3X	3	0.0691	0.0393	
Saskatoon Area	Solid	Swine	Surface	0X	3	0.0612	0.0234	
				1X	3	0.0256	0.0178	
				2X	3	0.0239	0.0239	
				3X	3	0.0622	0.0328	
Saskatoon Area	Liquid	Swine	Injected	0X	3	0.1198	0.0365	
				1X	3	1.1190	0.3310	
				2X	3	1.4830	0.1670	
				3X	3	2.2290	0.4250	
Saskatoon Area	Liquid	Swine	Surface	0X	2	0.0571	0.0571	1 outlier
				1X	3	0.0283	0.0186	
				2X	3	0.0186	0.0097	
				3X	2	0.0864	0.0455	1 outlier
Humboldt Area	Solid	Poultry	Injected	0X	3	0.0280	0.0078	
				1X	2	0.1373	0.0273	1 outlier
				2X	2	0.0555	0.0045	1 outlier
				3X	3	0.1448	0.0288	
Humboldt Area	Solid	Poultry	Surface	0X	3	0.0055	0.0055	
				1X	3	0.0081	0.0014	
				2X	2	0.0138	0.0018	1 outlier
				3X	2	0.0132	0.0016	1 outlier

Table I.6. N_2O data summary (with outliers).

Location	Type	Species	Mode	Rate	n	mean	stderr	Other information
U of S	Solid	Feedlot	Injected	0X	3	0.0324	0.0324	4 linear, 2 quadratic, 6 insignificant
				1X	3	0.0166	0.0118	1 quadratic significant but not used
				2X	3	0.0020	0.0020	
				3X	3	0.0142	0.0083	
U of S	Solid	Feedlot	Surface	0X	3	0.0086	0.0086	2 linear, 1 quadratic, 9 insignificant
				1X	3	0.0011	0.0011	
				2X	3	0.0051	0.0051	
				3X	3	0.0000	0.0000	
U of S	Liquid	Dairy	Injected	0X	6	0.0083	0.0022	13 linear, 0 quadratic, 2 insignificant
				1X	3	0.0116	0.0058	
				2X	3	0.0509	0.0134	
				3X	3	0.0375	0.0113	
U of S	Liquid	Dairy	Surface	0X	3	0.0060	0.0034	8 linear, 1 quadratic, 3 insignificant
				1X	3	0.0062	0.0031	
				2X	3	0.0103	0.0060	
				3X	3	0.0216	0.0129	
Saskatoon Area	Solid	Swine	Injected	0X	3	0.0299	0.0092	11 linear, 1 insignificant
				1X	3	0.0594	0.0114	1 quadratic significant but not used
				2X	3	0.1590	0.0818	
				3X	3	0.0691	0.0393	
Saskatoon Area	Solid	Swine	Surface	0X	3	0.0612	0.0234	8 linear, 1 quadratic, 3 insignificant
				1X	3	0.0256	0.0178	2 quadratic significant but not used
				2X	3	0.0239	0.0239	
				3X	3	0.0622	0.0328	
Saskatoon Area	Liquid	Swine	Injected	0X	3	0.1198	0.0365	12 linear
				1X	3	1.1190	0.3310	3 quadratic significant but not used
				2X	3	1.4830	0.1670	
				3X	3	2.2290	0.4250	
Saskatoon Area	Liquid	Swine	Surface	0X	3	0.2100	0.1560	9 linear, 1 quadratic, 2 insignificant
				1X	3	0.0283	0.0186	
				2X	3	0.0186	0.0097	
				3X	3	0.2420	0.1570	
Humboldt Area	Solid	Poultry	Injected	0X	3	0.0280	0.0078	7 linear, 5 quadratic
				1X	3	0.2570	0.1200	2 quadratic significant but not used
				2X	3	0.1760	0.1210	
				3X	3	0.1448	0.0288	
Humboldt Area	Solid	Poultry	Surface	0X	3	0.0055	0.0055	9 linear, 1 quadratic, 2 insignificant
				1X	3	0.0081	0.0014	1 quadratic significant but not used
				2X	3	0.0282	0.0145	
				3X	3	0.1041	0.0909	

Table I.7. CO_2 data summary (without outliers).

Location	Type	Species	Mode	Rate	n	mean	stderr	
U of S	Solid	Feedlot	Injected	0X	2	22.1	22.1	1 outlier
				1X	3	36.3	19.8	
				2X	3	20.7	11.0	
				3X	3	0.0	0.0	
U of S	Solid	Feedlot	Surface	0X	3	43.4	2.7	
				1X	3	12.9	12.9	
				2X	3	20.0	11.6	
				3X	3	13.6	1.5	
U of S	Liquid	Dairy	Injected	0X	6	82.1	19.7	
				1X	3	140.9	14.7	
				2X	3	241.0	39.3	
				3X	3	287.9	59.8	
U of S	Liquid	Dairy	Surface	0X	3	42.6	4.0	
				1X	3	137.9	39.9	
				2X	3	249.1	30.6	
				3X	2	96.1	86.1	1 outlier
Saskatoon Area	Solid	Swine	Injected	0X	3	50.5	15.4	
				1X	3	67.4	3.7	
				2X	3	147.3	10.8	
				3X	3	107.9	39.5	
Saskatoon Area	Solid	Swine	Surface	0X	3	47.5	6.6	
				1X	3	19.2	12.0	
				2X	3	85.0	4.6	
				3X	2	87.2	17.7	1 outlier
Saskatoon Area	Liquid	Swine	Injected	0X	3	111.3	64.4	
				1X	3	417.9	98.0	
				2X	3	683.0	151.0	
				3X	3	918.0	90.8	
Saskatoon Area	Liquid	Swine	Surface	0X	3	62.0	17.6	
				1X	3	155.9	89.4	
				2X	3	69.8	6.4	
				3X	2	242.7	53.1	1 outlier
Humboldt Area	Solid	Poultry	Injected	0X	3	57.9	8.3	
				1X	3	196.7	35.5	
				2X	3	129.3	73.8	
				3X	3	144.3	19.7	
Humboldt Area	Solid	Poultry	Surface	0X	3	24.5	13.5	
				1X	3	38.3	24.7	
				2X	2	107.3	58.4	1 outlier
				3X	3	99.5	34.2	

Table I.8. CO_2 data summary (with outliers).

Location	Type	Species	Mode	Rate	n	mean	stderr	Other information
U of S	Solid	Feedlot	Injected	0X	3	72.8	52.3	6 linear, 6 insignificant
				1X	3	36.3	19.8	1 quadratic significant but not used
				2X	3	20.7	11.0	
				3X	3	0.0	0.0	
U of S	Solid	Feedlot	Surface	0X	3	43.4	2.7	9 linear, 3 insignificant
				1X	3	12.9	12.9	1 quadratic significant but not used
				2X	3	20.0	11.6	
				3X	3	13.6	1.5	
U of S	Liquid	Dairy	Injected	0X	6	82.1	19.7	14 linear, 1 quadratic
				1X	3	140.9	14.7	4 quadratic significant but not used
				2X	3	241.0	39.3	
				3X	3	287.9	59.8	
U of S	Liquid	Dairy	Surface	0X	3	42.6	4.0	10 linear, 1 quadratic, 1 insignificant
				1X	3	137.9	39.9	
				2X	3	249.1	30.6	
				3X	3	241.0	162.0	
Saskatoon Area	Solid	Swine	Injected	0X	3	50.5	15.4	11 linear, 1 quadratic
				1X	3	67.4	3.7	3 quadratic significant but not used
				2X	3	147.3	10.8	
				3X	3	107.9	39.5	
Saskatoon Area	Solid	Swine	Surface	0X	3	47.5	6.6	7 linear, 4 quadratic, 1 insignificant
				1X	3	19.2	12.0	
				2X	3	85.0	4.6	
				3X	3	124.5	38.7	
Saskatoon Area	Liquid	Swine	Injected	0X	3	111.3	64.4	11 linear, 1 insignficant
				1X	3	417.9	98.0	3 quadratic significant but not used
				2X	3	683.0	151.0	
				3X	3	918.0	90.8	
Saskatoon Area	Liquid	Swine	Surface	0X	3	62.0	17.6	9 linear, 2 quadratic, 1 insignificant
				1X	3	155.9	89.4	3 quadratic significant but not used
				2X	3	69.8	6.4	
				3X	3	366.0	127.0	
Humboldt Area	Solid	Poultry	Injected	0X	3	57.9	8.3	8 linear, 3 quadratic, 1 insignificant
				1X	3	196.7	35.5	1 quadratic significant but not used
				2X	3	129.3	73.8	
				3X	3	144.3	19.7	
Humboldt Area	Solid	Poultry	Surface	0X	3	24.5	13.5	9 linear, 1 quadratic, 2 insignificant
				1X	3	38.3	24.7	1 quadratic significant but not used
				2X	3	164.2	66.1	
				3X	3	99.5	34.2	

Table I.9. CH_4 data summary (insignificants as missing).

Location	Type	Species	Mode	Rate	n	mean	stderr
U of S	Solid	Feedlot	Injected	0X	0	-	-
				1X	1	-0.424	-
				2X	1	-0.328	-
				3X	0	-	-
U of S	Solid	Feedlot	Surface	0X	0	-	-
				1X	0	-	-
				2X	0	-	-
				3X	0	-	-
U of S	Liquid	Dairy	Injected	0X	3	-0.026	0.027
				1X	1	0.003	0.015
				2X	1	0.105	0.015
				3X	0	0.198	0.057
U of S	Liquid	Dairy	Surface	0X	1	-0.053	-
				1X	2	0.041	0.004
				2X	1	0.130	-
				3X	1	-0.131	-
Saskatoon Area	Solid	Swine	Injected	0X	0	-	-
				1X	2	-0.161	0.096
				2X	0	-	-
				3X	2	0.005	0.264
Saskatoon Area	Solid	Swine	Surface	0X	3	0.211	0.074
				1X	2	0.091	0.009
				2X	2	0.112	0.078
				3X	1	0.045	-
Saskatoon Area	Liquid	Swine	Injected	0X	1	0.115	-
				1X	1	0.017	-
				2X	1	0.121	-
				3X	0	-	-
Saskatoon Area	Liquid	Swine	Surface	0X	1	-0.159	-
				1X	0	-	-
				2X	0	-	-
				3X	1	0.004	-
Humboldt Area	Solid	Poultry	Injected	0X	2	0.136	0.078
				1X	1	0.014	-
				2X	1	0.063	-
				3X	1	0.017	-
Humboldt Area	Solid	Poultry	Surface	0X	2	-0.113	0.067
				1X	2	-0.155	0.051
				2X	1	-0.048	-
				3X	1	-0.075	-

Table I.10. CH_4 data summary (insignificants as zero).

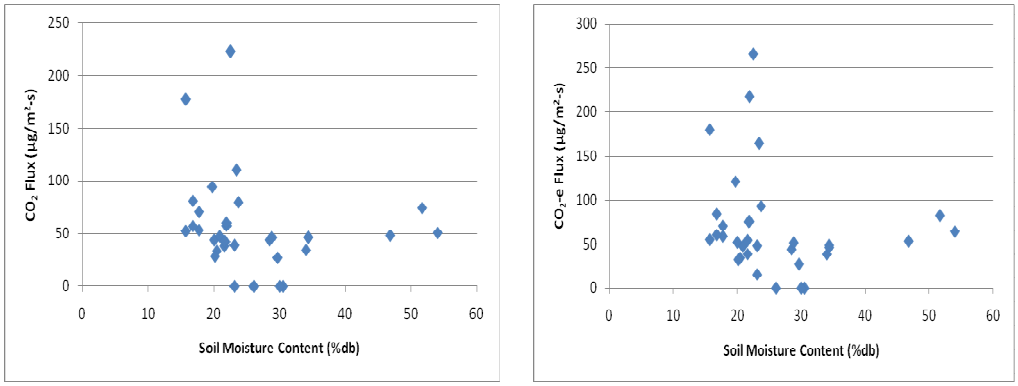
Location	Type	Species	Mode	Rate	n	mean	stderr
U of S	Solid	Feedlot	Injected	0X	3	0.000	0.000
				1X	3	-0.141	0.141
				2X	3	-0.109	0.109
				3X	3	0.000	0.000
U of S	Solid	Feedlot	Surface	0X	3	0.000	0.000
				1X	3	0.000	0.000
				2X	3	0.000	0.000
				3X	3	0.000	0.000
U of S	Liquid	Dairy	Injected	0X	6	-0.013	0.014
				1X	3	0.002	0.009
				2X	3	0.070	0.036
				3X	3	0.199	0.057
U of S	Liquid	Dairy	Surface	0X	3	-0.015	0.015
				1X	3	0.027	0.014
				2X	3	0.043	0.043
				3X	3	-0.004	0.004
Saskatoon Area	Solid	Swine	Injected	0X	3	0.000	0.000
				1X	3	-0.107	0.769
				2X	3	0.000	0.000
				3X	3	0.003	0.152
Saskatoon Area	Solid	Swine	Surface	0X	3	0.211	0.074
				1X	3	0.061	0.031
				2X	3	0.075	0.059
				3X	3	0.015	0.015
Saskatoon Area	Liquid	Swine	Injected	0X	3	0.038	0.038
				1X	3	0.006	0.006
				2X	3	0.040	0.040
				3X	3	0.000	0.000
Saskatoon Area	Liquid	Swine	Surface	0X	3	-0.053	0.053
				1X	3	0.000	0.000
				2X	3	0.000	0.000
				3X	3	0.001	0.001
Humboldt Area	Solid	Poultry	Injected	0X	3	0.091	0.064
				1X	3	0.005	0.005
				2X	3	0.021	0.021
				3X	3	0.006	0.006
Humboldt Area	Solid	Poultry	Surface	0X	3	-0.075	0.054
				1X	3	-0.104	0.060
				2X	3	-0.016	0.016
				3X	3	-0.025	0.025

Table I.11. CO_2-e data summary (without outliers).

Location	Type	Species	Mode	Rate	n	mean	stderr	
U of S	Solid	Feedlot	Injected	0X	2	22.10	3.18	1 outlier
				1X	3	41.40	40.50	
				2X	3	21.30	32.40	
				3X	3	4.39	86.20	
U of S	Solid	Feedlot	Surface	0X	3	46.11	22.10	
				1X	3	13.20	22.30	
				2X	3	21.60	11.10	
				3X	3	13.62	2.57	
U of S	Liquid	Dairy	Injected	0X	6	84.70	19.50	
				1X	3	144.50	16.20	
				2X	3	256.70	40.50	
				3X	3	299.50	62.80	
U of S	Liquid	Dairy	Surface	0X	3	44.49	3.18	
				1X	3	139.80	40.50	
				2X	3	252.30	32.40	
				3X	2	88.80	86.20	1 outlier
Saskatoon Area	Solid	Swine	Injected	0X	3	59.70	17.80	
				1X	3	85.79	4.09	
				2X	3	196.50	15.40	
				3X	3	129.30	50.50	
Saskatoon Area	Solid	Swine	Surface	0X	3	66.48	9.17	
				1X	3	27.13	8.25	
				2X	3	92.37	8.57	
				3X	2	98.90	29.40	1 outlier
Saskatoon Area	Liquid	Swine	Injected	0X	3	148.40	72.60	
				1X	3	787.00	198.00	
				2X	3	1143.00	196.00	
				3X	3	1609.00	207.00	
Saskatoon Area	Liquid	Swine	Surface	0X	3	124.00	53.00	
				1X	3	164.70	94.70	
				2X	3	75.58	9.35	
				3X	2	269.50	67.20	1 outlier
Humboldt Area	Solid	Poultry	Injected	0X	3	66.55	8.43	
				1X	2	203.74	7.83	1 outlier
				2X	3	184.00	108.00	
				3X	3	189.10	16.30	
Humboldt Area	Solid	Poultry	Surface	0X	3	26.20	14.90	
				1X	3	40.80	24.90	
				2X	2	118.00	65.40	1 outlier
				3X	2	70.30	13.00	1 outlier

Table I.12. CO_2-e data summary (with outliers).

Location	Type	Species	Mode	Rate	n	mean	stderr
U of S	Solid	Feedlot	Injected	0X	3	82.90	62.10
				1X	3	41.40	40.50
				2X	3	21.30	32.40
				3X	3	4.39	86.20
U of S	Solid	Feedlot	Surface	0X	3	46.11	22.10
				1X	3	13.20	22.30
				2X	3	21.60	11.10
				3X	3	13.62	2.57
U of S	Liquid	Dairy	Injected	0X	6	84.70	19.50
				1X	3	144.50	16.20
				2X	3	256.70	40.50
				3X	3	299.50	62.80
U of S	Liquid	Dairy	Surface	0X	3	44.49	3.18
				1X	3	139.80	40.50
				2X	3	252.30	32.40
				3X	3	247.00	166.00
Saskatoon Area	Solid	Swine	Injected	0X	3	59.70	17.80
				1X	3	85.79	4.09
				2X	3	196.50	15.40
				3X	3	129.30	50.50
Saskatoon Area	Solid	Swine	Surface	0X	3	66.48	9.17
				1X	3	27.13	8.25
				2X	3	92.37	8.57
				3X	3	143.80	48.00
Saskatoon Area	Liquid	Swine	Injected	0X	3	148.40	72.60
				1X	3	787.00	198.00
				2X	3	1143.00	196.00
				3X	3	1609.00	207.00
Saskatoon Area	Liquid	Swine	Surface	0X	3	124.00	53.00
				1X	3	164.70	94.70
				2X	3	75.58	9.35
				3X	3	441.00	176.00
Humboldt Area	Solid	Poultry	Injected	0X	3	66.55	8.43
				1X	3	276.20	72.60
				2X	3	131.70	61.90
				3X	3	189.10	16.30
Humboldt Area	Solid	Poultry	Surface	0X	3	26.20	14.90
				1X	3	40.80	24.90
				2X	3	118.00	65.40
				3X	3	70.30	13.00



(a) (b)

Figure I.1. Effect of soil moisutre content on background a) CO_2 and b) CO_2-e fluxes.

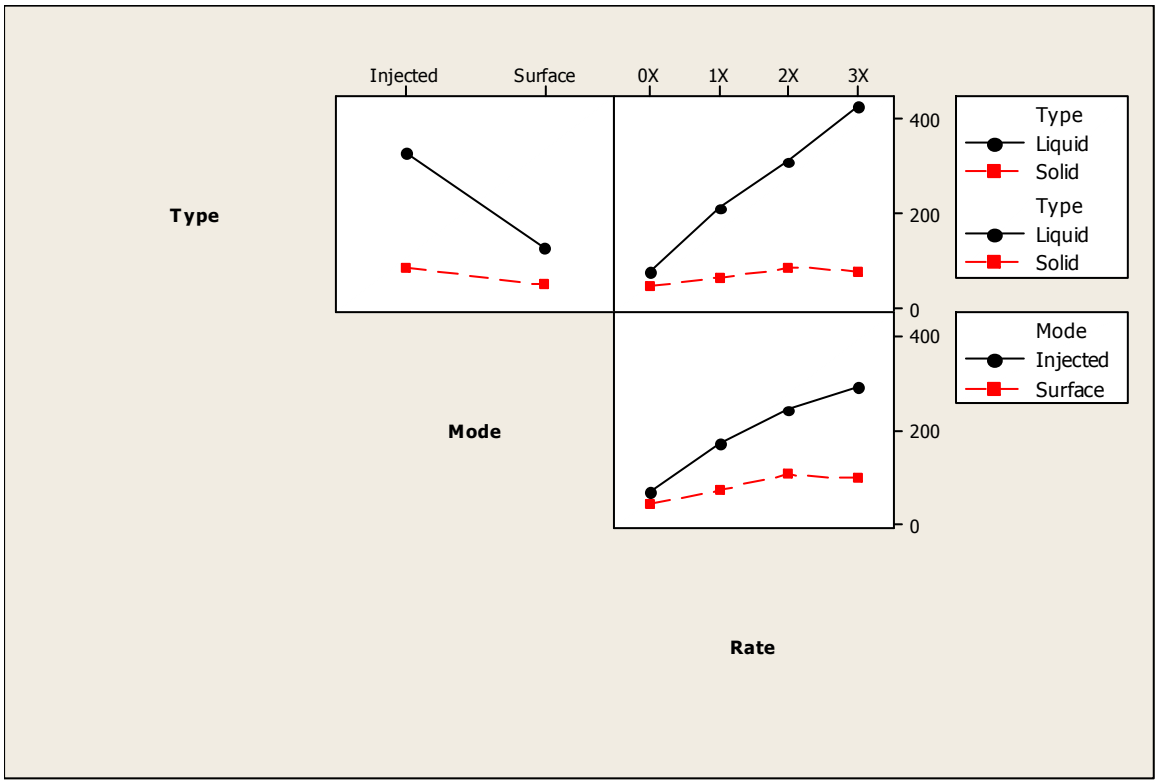


Figure I.2. Interactions plots for CO_2 flux. All interactions were statistically significant (P=0.000 for type*mode, P=0.001 for type*rate, P=0.024 for mode*rate and P=0.019 for type*mode*rate). Interaction trends and significances were very similar for CO_2-e and N_2O fluxes.

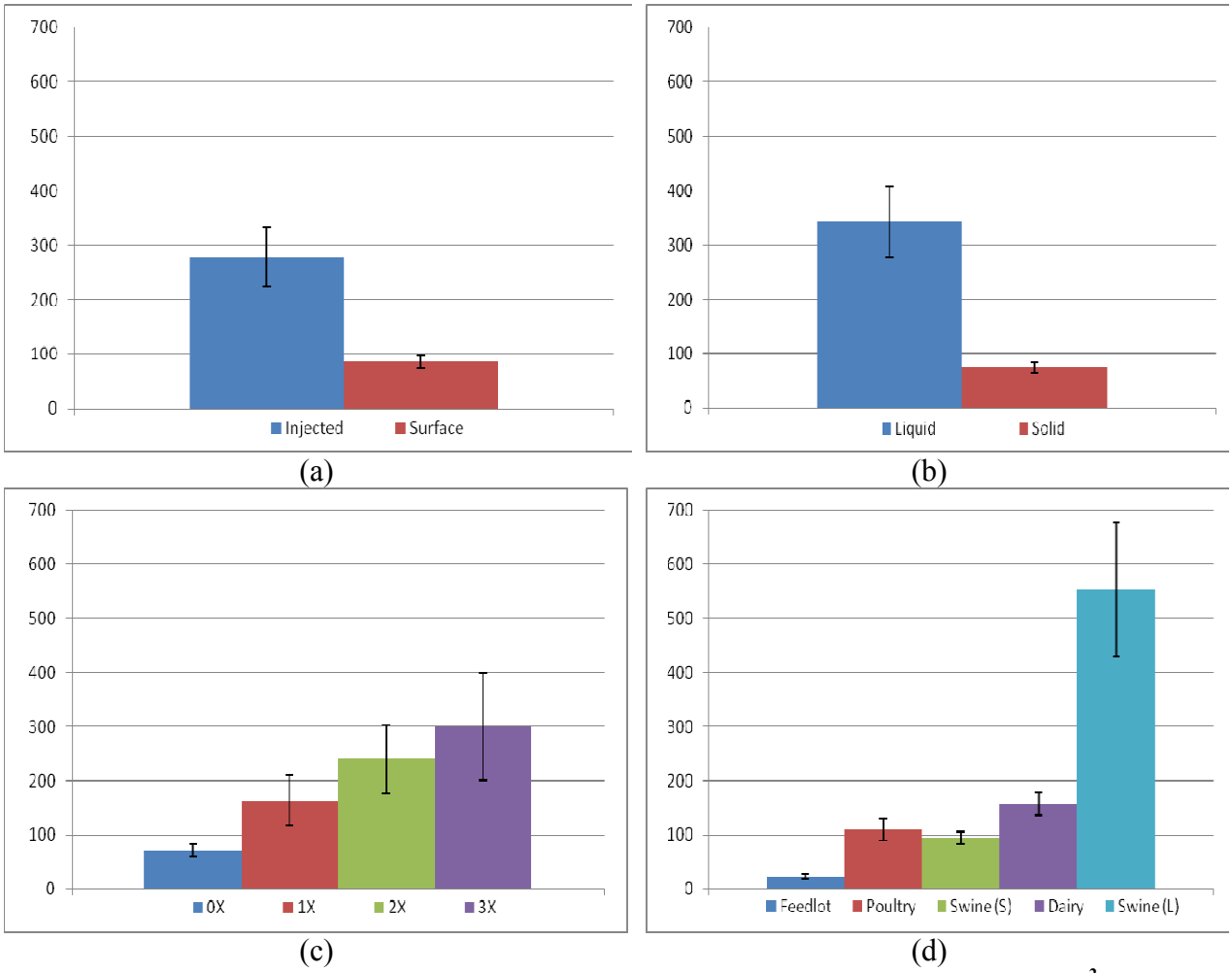


Figure I.3. Graphical summary of absolute CO_2-e fluxes. Vertical axes represent CO_2-e flux ($\mu g/m^2$-s). (a) Effect of application method, (b) effect of manure type, (c) effect of application rate, (d) effect of manure species.

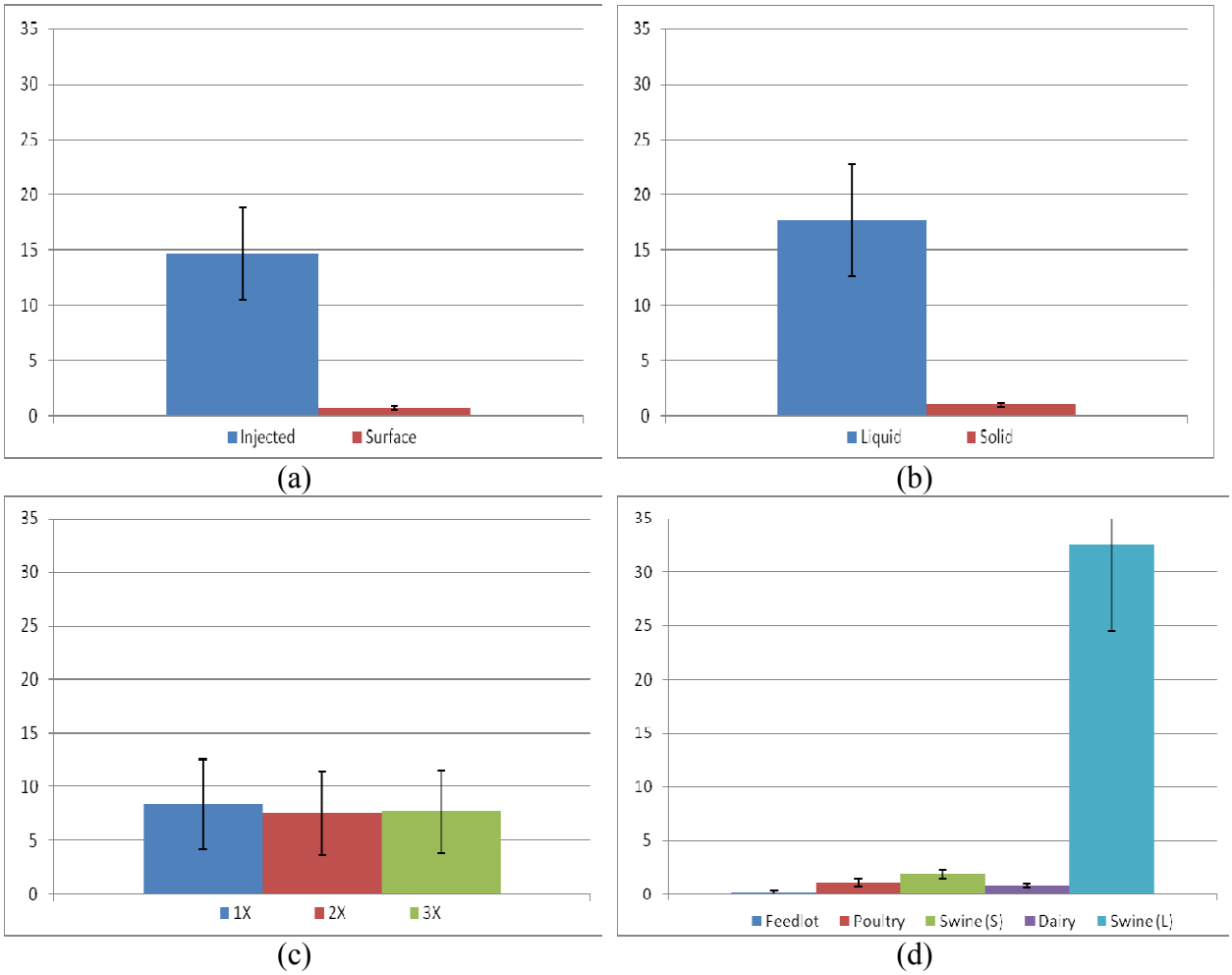


Figure I.4. Treatment effects on mean specific N_2O fluxes (µg N_2O/kg N applied/s). (a) Effect of application method, (b) effect of manure type, (c) effect of application rate, and (d) effect of manure species.

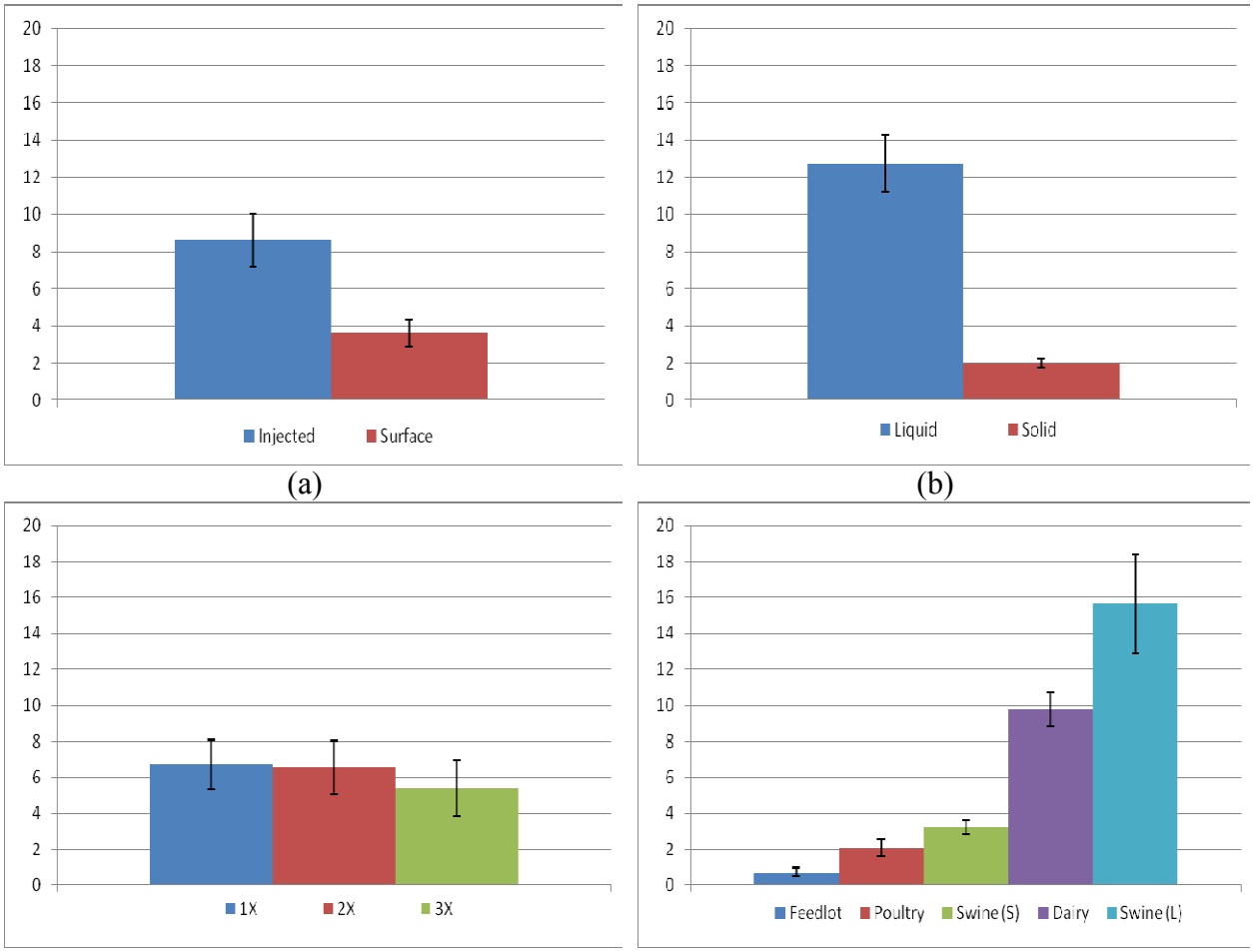
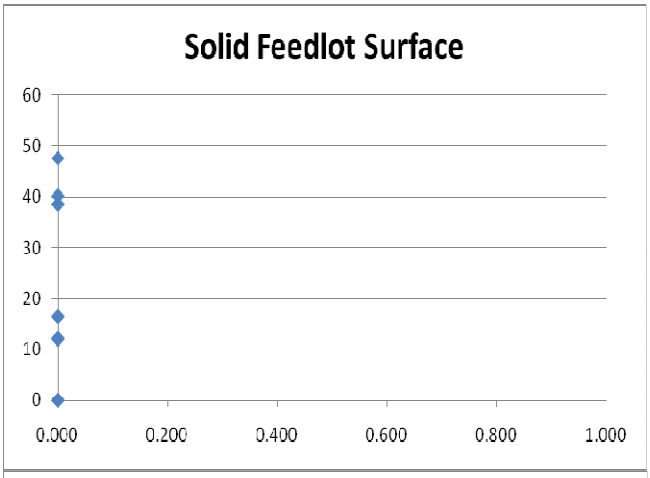
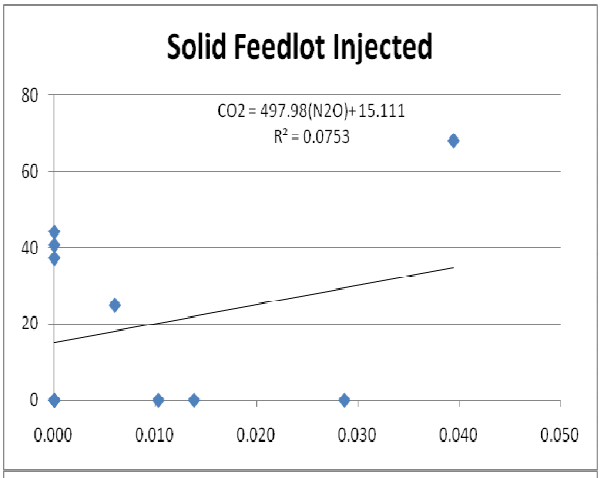
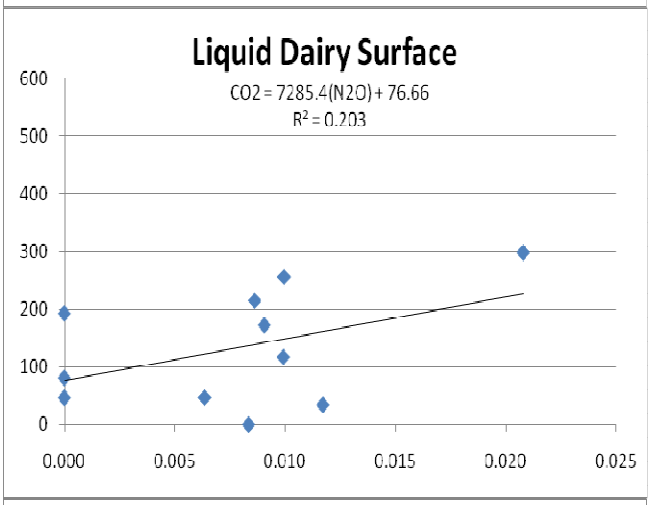
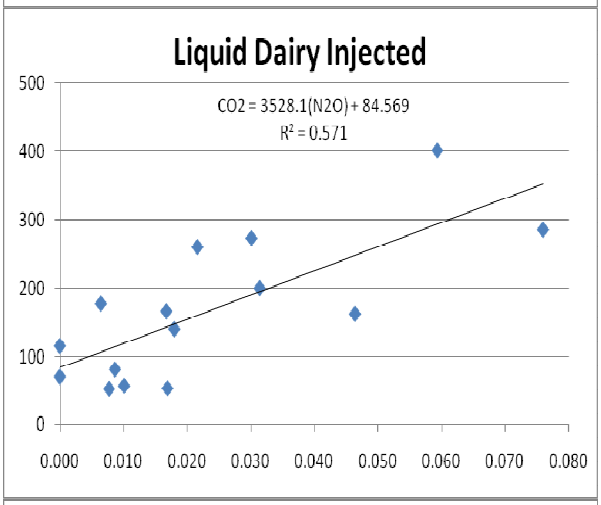


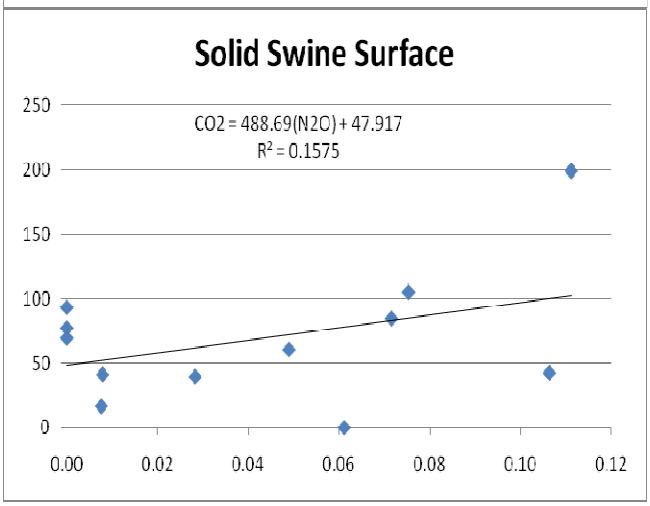
Figure I.5. Treatment effects on mean specific CO_2 fluxes (mg CO_2/kg N applied/s). (a) Effect of application method, (b) effect of manure type, (c) effect of application rate, and (d) effect of manure species.

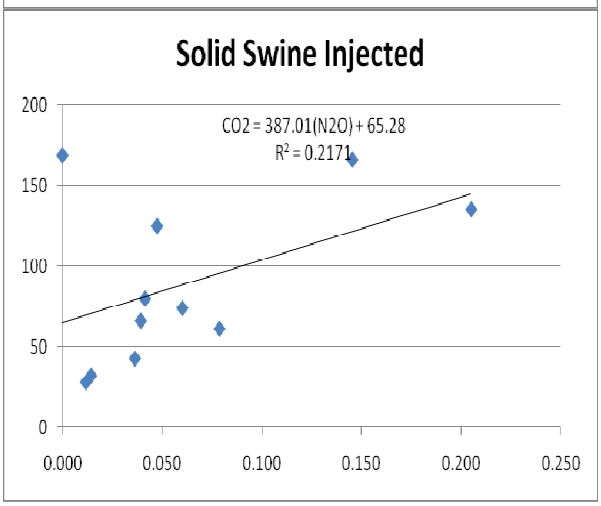

Solid Feedlot Surface
60
50
40
30
20
10
0
0.000
0.200
0.400
0.600
0.800
1.000


Solid Feedlot Injected
CO2 = 497.98(N2O) + 15.111
R² = 0.0753
80
60
40
20
0
0.000
0.010
0.020
0.030
0.040
0.050


Liquid Dairy Surface
CO2 = 7285.4(N2O) + 76.66
R² = 0.203
600
500
400
300
200
100
0
0.000
0.005
0.010
0.015
0.020
0.025


Liquid Dairy Injected
CO2 = 3528.1(N2O) + 84.569
R² = 0.571
500
400
300
200
100
0
0.000
0.010
0.020
0.030
0.040
0.050
0.060
0.070
0.080


Solid Swine Surface
CO2 = 488.69(N2O) + 47.917
R² = 0.1575
250
200
150
100
50
0
0.00
0.02
0.04
0.06
0.08
0.10
0.12


Solid Swine Injected
CO2 = 387.01(N2O) + 65.28
R² = 0.2171
200
150
100
50
0
0.000
0.050
0.100
0.150
0.200
0.250

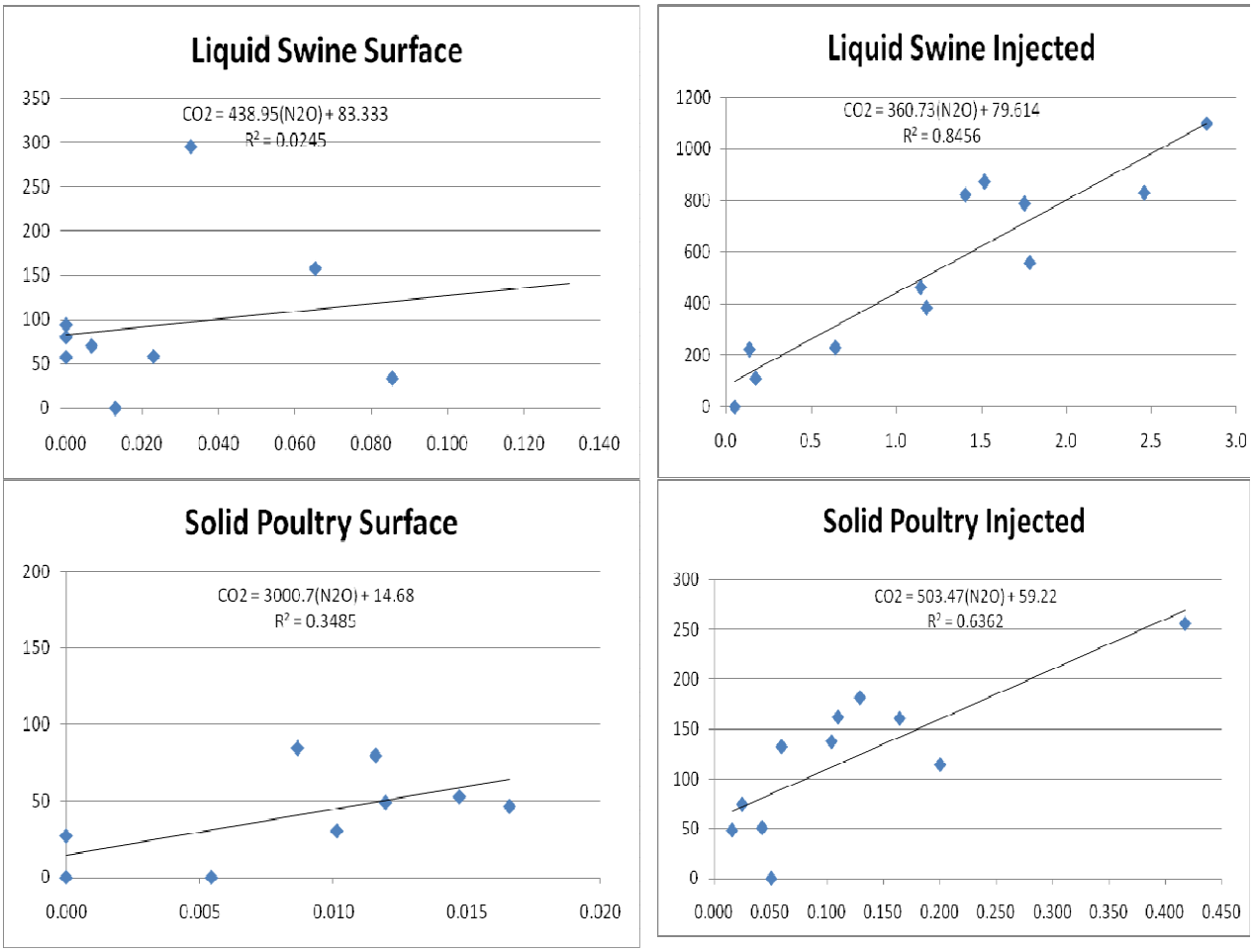


Figure I.6. Correlation of CO_2 and N_2O fluxes based on manure type and application method. Vertical axes represent CO_2 flux (µg/m^2-s).and horizontal axes represent N_2O flux (µg/m^2-s). Note the different scales for both CO_2 and N_2O flux among different treatments.

Chapter 5

5.0 Prediction of Odour Emission Rate after Land Application of Manure

The measurement or modelling of emission rate trends is essential for the application of dispersion models which can help to optimize separation distances between manure spreading activities and neighbours. The model parameters for an existing volatilization model were determined from field and literature data and the resulting model allowed the effects of application mode (surface vs. subsurface) and manure type (liquid vs. solid) on odour emissions to be simulated. The effects of injection depth and a coverage factor on emissions were also simulated. The modeled peak fluxes from liquid manure applications were higher than those for solid manure applications, but the extended duration of odour emissions for solid manure resulted in higher cumulative losses of odour from solid manure applications. While the application rate had no effect on the initial odour flux, higher application rates resulted in higher peak fluxes, higher overall emissions, and longer odour durations for both manure types and application methods. In general, the ranking of cumulative odour emissions was: solid surface > liquid surface >> liquid injected > solid injected. When typical coverage factors were assumed, the percent reduction in cumulative odours due to injection were approximately 75, 55, and 30% for liquid manure at 1X, 2X, and 3X application rates, respectively and 90, 80, and 70% for solid manure. Injection depths as low as 0.05 m (5 cm) were shown by the model to significantly reduce odours from both liquid and solid manure applications compared to surface spreading. The general predictions of the model developed in this study agree with odour emission rate trends and percent reductions of odour due to injection reported in literature. Future work should

focus on better estimation of the model parameters and the variation of effective diffusivity with time and soil conditions.

5.1 Introduction

In order to allow for the sustainable growth of the livestock industry, management practices that reduce or control the odour emissions associated with livestock production must be adopted. Livestock odours are commonly recognized to come from three main sources: production buildings, manure storages, and land application of manure. There has been considerable research on measuring emissions and estimating the dispersion of odours from buildings and manure storages, but little effort has been spent on modeling the dispersion of odours from land application activities. While manure spreading produces odours of short duration, they are considered more intense and more unpleasant than odours from the barns or manure storages. In fact, more than half of all complaints about intensive livestock facilities directly result from odour emissions following land application of manure (Choinière et al., 2007). Mkhabela et al. (2008) also noted that land spreading of manure draws more complaints about nuisance odour than any other aspect of livestock production (AAFC, 1998; Philips et al., 1991 in: Mkhabela et al., 2008). Specific management practices such as subsurface application of manure have been shown to reduce the odour emissions immediately after application (refer to Chapter 3). In order to predict the impact of these practices on odour surrounding application sites using dispersion models, reliable odour emission rates from the source are required. Source emission rates from manure spreading will vary over the first few hours after application and the magnitude and variation will depend on the type of manure, application rate and application method. This information is currently unavailable and is required to apply dispersion modeling to manure spreading activities.

Traditional methods of odour measurement (wind tunnels, steady-state chambers, Nasal Rangers$^{(TM)}$) make it difficult to measure odour variation over time. Micrometeorological methods have been adapted for use in odour measurement studies (Pain et al., 1991; Mkhabela et al., 2007, Huijsmans et al., 2001), but a full assessment of the impact of management activities

on odour emissions over time after application would require a large and costly experimental design. A modeling approach may be a more prudent way to gather information on the impacts of application method, application rate, and manure type on the odour emission rate variation over time after application. Process-based modeling with computer simulation is a cost-effective procedure for quantifying and evaluating emissions across diverse production systems (Montes et al., 2009).

If the odour emission rate trend over the first few hours after manure application with different methods and manure types can be reliably predicted, then dispersion models (such as the Gaussian ISC model or INPUFF model (Xing et al., 2006) can be used to establish set-back distances for manure spreading. This will minimize the odour nuisance to neighbours while maximizing land-use efficiency. Therefore, the objectives of this work were 1) to review existing emission rate models and conduct further model development using data and insight gathered in a field study of odour emissions and 2) to assess the applicability of the developed model in estimating the effects of manure type, application mode, and application rate on the odour emission rate trend over time after application.

5.2 Literature Review

5.2.1 Emission rate models

A review of literature discussing modeling of emissions from a surface revealed very few references to odour emission rate models. The majority of work related to manure emissions dealt with ammonia and there were several well developed mechanistic models that predicted emissions of volatile organic compounds (VOC's) from landfills. Some of these landfill models accounted for a covering material over the landfill and allowed for constant or variable source emissions. Other models dealt with VOC emissions from aeration basins or building materials.

5.2.1.1 Ammonia emission models

Ni (1999) provided a very good review of several mechanistic models of ammonia (NH_3) release from liquid manure, including ammonia release from slurry applied fields. All of the ammonia release models discussed were developed on the basis of some physical insight such as the enzymatic and microbial generation of NH_3, the diffusion mass transfer of NH_3 in manure, the chemistry of NH_3 in aqueous solution, and the convective mass transfer of NH_3 gas from the manure surface into the free air stream (Ni, 1999). The paper reviewed the general structure and elements of 30 existing models for ammonia emissions but did not specifically discuss the application of models to emissions from manure spreading. The author did note that the determination of the convective mass transfer coefficient is essential in developing an accurate NH_3 emission model (Ni, 1999).

Mansel et al. (2005) developed a process-based (empirical) model to estimate the ammonia emissions from an entire livestock facility, including a submodel to account for ammonia emissions from the land application of manure. While the authors compared the results of their full process-based approach with the GIS-based ammonia emission model developed for the Western Regional Air Partnership (WRAP) model, they did not reveal the details or validation results from the land application submodel. The authors noted that ammonia emissions from land application depend on type of manure, crop management practices and climatic conditions. In order to use the land application submodel, data regarding the nutrient content of the manure, specific application and crop management practices, and environmental conditions are required.

Menzi et al. (1998) presented an empirical model for ammonia emissions after manure application. The effects of manure dry matter content, total ammoniacal nitrogen (TAN), application rate, and solar radiation on emissions were studied with wind tunnel experiments. Their regression analysis related emission rate (kg NH_3-N/ha) with TAN, application rate and saturation deficit (where saturation deficit is related to relative humidity (RH) and temperature). This empirical model is valid only for the conditions under which the data were collected. This experiment and empirical model did not indicate a significant relationship between dry matter content and NH_3 emissions, probably due to the low level and small range of dry matter contents used in this study (Menzi et al., 1998).

Misselbrook et al. (2005) also developed an empirical model to predict ammonia losses following application of manure. The authors noted that the key parameters driving ammonia emissions after manure spreading were the wind speed, dry matter content for slurries, and rainfall for solid manures. For each experiment, the cumulative NH_3 loss with time was fitted with a Michaelis-Menten type curve:

$$N(t) = N_{\max} \frac{t}{t + K_m} \tag{5.1}$$

where N(t) is the cumulative loss at time t (kg N/ha), and N_{max} and K_m are model parameters representing total loss as time approaches infinity and time at which loss reaches one half of maximum, respectively.

Although application rate was not a key parameter in their study, Misselbrook et al. (2005) noted that increasing slurry application rate had been shown to decrease the proportion of TAN emitted as NH_3 according to Frost (1994) and Thompson et al. (1990) due to the decreased surface area to volume ratio for higher application rates (Misselbrook et al., 2005). The same researchers also suggested that rapid mineralization during the measurement period increased the potential for NH_3 loss from solid manure application sites (Misselbrook et al., 2005).

Plöchl (2001) presented a neural network approach for modelling ammonia emissions after manure spreading. The author used published data to train the neural network and determine the empirical constants N_{max} and K_m for the Michaelis-Menten function. Input parameters of the neural network included DM, pH, ammonium concentration, ammonium applied, vegetation type, minimum temperature, maximum temperature, precipitation, wind speed, and irradiation. Plöchl (2001) theorized that two steps control the kinetics of the ammonia emission process: desorption from the surface and diffusive transport across the boundary layer. These processes are functions of manure pH, wind velocity at the surface, surface area and surface characteristics, and air and manure temperature. In this analysis, no comparison of application methods was made because of the low availability of data sets reflecting the differences in emission due to different application methods (Plöchl, 2001). In order to determine the effects of incorporating or injecting manure, it is essential to understand the dynamics of the emissions from the soil

surface. It is not yet clear whether incorporation of manure into the soil affects only the maximum emission (N_{max}) or if these methods also affect the emission dynamics, which would be expressed in a change of the K_m value (Plöchl, 2001).

Génermont and Cellier (1997) presented a mechanistic model for ammonia volatilization from manure application that combines an atmospheric transfer model with a model of the soil processes responsible for the release of ammonia to the atmosphere. The model accounts for the physical and chemical equilibria in each soil layer, heat and water transfers between the soil layers, aqueous and gaseous ammoniacal N transfers between the soil layers and transfer of ammonia gas to the atmosphere. The model uses readily available input data including soil, meteorological and slurry data. In this model, it was assumed that the physical properties of the soil did not change with time after the slurry has been spread. Depending on the soil and manure type and the application rate, this assumption may not be valid. Also, since ammonia volatilization occurs over a short time (2-3 weeks), nitrogen transformations by organic matter and organic N mineralization, uptake by plants, oxidation or nitrification were not accounted for (Génermont and Cellier, 1997). The researchers tested the model against data collected from a field study (dairy cattle slurry applied at a rate of 133 m^3/ha or 114 kg N/ha) where micrometeorological methods were used to measure ammonia fluxes over 10 days after application of slurry. The calculated loss was 57 kg/ha and measured loss was 62 kg/ha. In general, the predicted fluxes on the first day were underestimated. However, the surface areas of manure patches and droplets were not constant, and the varying manure pH (an effect of emission itself) were not consistent with the model assumptions (Plöchl, 2001).

5.2.1.2 Volatile organic compound emission models

In contrast to the ammonia emission models, almost all models discussing volatile organic compound (VOC) emissions from landfills found in literature were mechanistic models. Most volatilization models included a convective mass transfer model and involved Henry's Law which relates the concentration of dissolved compounds in water to an equilibrium concentration of the compound in the air space immediately above the solution.

Several of the VOC emission models accounted for a covering layer through which compounds must first diffuse before they volatilize into the atmosphere. Additionally, some landfill models assumed a constant VOC generation term but others used an exponentially decaying model to describe the VOC generation term.

Rotenberg and Mamane (1998) provided a very detailed discussion of a model for estimating emissions of VOC's from landfills. Their model described a landfill as two uniform layers including the waste layer and the soil cover. Several assumptions were made in the development of the model:

- Gas movement is only in upward direction
- Bottom layer is impervious (no leaching)
- Rapid removal of gases takes place at upper surface by wind
- VOC's are continuously and uniformly produced in the waste layer
- VOC generation is the net difference between production and removal within the waste layer
- Diffusion coefficients are assumed constant within a particular layer (in reality, diffusion coefficients are time and space dependent and depend on soil temperature, water content, meteorological conditions and composition of the soil cover layer)
- No gases accumulate in the cover layer (rate of diffusion from the soil cover is faster than from the waste layer)
- All gases entering the soil cover from the waste layer reach the atmosphere (emission rate from waste layer = emission rate from soil cover)
- The concentration of VOCs at the interface between the waste and the air space in the soil cover layer can be described using Henry's Law

For the case where the waste is covered with a soil layer additional assumptions are needed:

- There is no change in VOC's concentration at the bottom of the waste layer
- VOC concentration at the interface may be described by Henry's Law
- Initial VOC's concentration is the same all around the waste layer

This model was applied to emissions from an exposed waste layer and emissions from a covered waste layer. In addition, the model used both a constant production rate and a rate that decreased exponentially with time. The time scale for this model was very long, up to 4,000 days.

Karimi et al. (1986, 1988) presented another model describing emissions of VOC's from landfills where different types of covers were present. The model is based on the model used by Farmer et al. (1980), which is based on the theory of flow through porous media and accounts for the diffusion transport and volatilization of the pollutants. The vapour flux of the pollutant is determined from Fick's first law that states the diffusion flux is equal to the product of diffusivity and concentration gradient. The required inputs include the concentrations of the pollutant in the air at the bottom of the waste layer and the surface of the soil, the thickness of the soil layer and the apparent diffusivity of the volatile pollutant (Karimi et al., 1986).

Karimi et al. (1988) discussed the application of this model to a landfill covered by different composite materials. The model as presented represents a single-layer soil cover but the authors extended the model for estimation of volatilization flux through composite, two-layer covers. Karimi et al. (1988) identified various factors that control emissions through soil covers such as the soil bulk density, water content, total porosity, and air filled porosity as well as volatility characteristics of VOC's. The equation for mass flux (g/cm^2-s) included the following variables:

- Depth of soil layer (cm)
- Molecular weight of component (g/mol)
- Total pressure (atm)
- Partial pressures of component at bottom and top of soil (atm)
- Universal gas constant (L atm/K-mol)
- Absolute temp (K)
- Apparent vapor diffusion coefficient of component in soil (cm^2/s)

Karimi et al. (1988) noted that the emission flux was dependent on two important variables: the volatility of the VOC indicated by its vapor pressure and the molecular diffusivity of VOC through the air.

Lin and Hildemann (1995) presented a very complex, nonsteady-state model for VOC emissions from landfills that accounted for biogas flow, leachate flow, diffusion, adsorption, degradation, volatilization, and mass transfer limitations through a top cover. In other models, the required assumptions oversimplify the landfill environment and cause the emission rate to be overestimated since, in addition to the gas route, contaminants can also dissolve into leachate and be carried away (Lin and Hildemann, 1995). Furthermore, lab studies have shown that the emission rate is unsteady (Rickabaugh and Kinman, 1993). Lin and Hildemann (1995) also recognized that contaminants in the subsurface can be present in a vapour, liquid, solid, or adsorbed phase. The extent of adsorption depends greatly on the moisture content of the soil; volatile compounds adsorb most strongly to soil under conditions where the moisture content is low (Lin and Hildemann, 1995). In addition to oxidation of VOC's in the cover layer, adsorption is assumed to be one of the mechanisms that result in lower emission rates from covered landfills. However, while reducing the emission rate, adsorption results in prolonged emission duration (Lin and Hildemann, 1995). The authors noted that adsorption coefficients and effective diffusivities are the most difficult parameters to estimate accurately, especially since adsorption coefficients within dry systems have only recently begun to become available.

The input parameters for the model described in Lin and Hildemann (1995) included:

- Landfill characteristics
    - Cover depth, bulk density of soil, volumetric air content, volumetric water content
- Chemical properties
    - Gaseous diffusivity in soil, aqueous diffusivity in soil, gaseous diffusivity in cover, overall first order degradation rate, gas/solid adsorption coefficient, liquid/solid adsorption coefficient, Henry's Law constant
- Field measurements
    - Bulk gas velocity, bulk leachate velocity, mass transfer coefficient, (per day) concentration gradients, etc.

Generally, the above models performed well in their prediction of VOC diffusion and volatilization into the atmosphere. The model in Karimi et al. (1986) was successfully used in the design of landfill covers while the model in Rotenberg and Mamane (1998) allowed the

estimation of the effects of landfill covers on VOC emission rates in the first few years of operation. The complex model presented in Lin and Hildemann (1995) allowed for modeling of VOC movement in landfills in three dimensions as well as the prediction of changes in subsurface concentrations and emission fluxes with times based on different initial physical and chemical conditions.

5.2.1.3 Organic chemical movement in soil

A mathematical model presented by Jury et al. (1983, 1984a, 1984b, 1984c, 1990) described the transport and loss of soil-applied organic chemicals. Later versions of the model included movement of organic compounds by vapor or liquid diffusion and mass flow through a soil layer devoid of the same chemical (Jury et al., 1990). While diffusing through the soil layer, it was assumed that the compounds undergo first-order degradation and linear equilibrium adsorption while loss to the atmosphere is governed by vapor diffusion through a stagnant air boundary layer (Jury et al., 1990). The model was intended to help classify organic chemicals for their relative susceptibility to different loss pathways including volatilization, leaching, and degradation (Jury et al., 1983). The authors stated that, although the model was designed to predict the movement of pesticides, it was applicable to other trace organics that may be of environmental concern (Jury et al., 1983).

The Jury model assumed that compounds exist in three phases within the soil matrix: adsorbed, liquid and gaseous. Prediction of how the applied chemical would partition between these three phases in soil was achieved by defining expressions for the adsorbed-liquid partitioning and the liquid-vapour partitioning. The adsorbed-liquid partitioning expression was partially dependent on the soil organic matter content while the liquid-vapour partitioning expression was represented through Henry's Law.

The degradation rate was defined as a direct assessment of the persistence of a compound (Jury et al., 1983). A net, first-order degradation rate was assumed for all degradative processes in all phases. The first-order degradation rate constant (μ, per day) was related to the half life ($T_{1/2}$, day) of the compound by:

$$\mu = \frac{\ln(2)}{T_{1/2}} \tag{5.2}$$

The authors noted that temperature, water content, and microbial populations could also influence degradation processes and measured rate constants considerably. Thus, this property was deemed both extremely important and extremely difficult to assess (Jury et al., 1983).

A mass balance was applied in Jury et al. (1983), assuming a one-dimensional, homogeneous porous medium undergoing first-order decay:

$$\frac{\partial C_T}{\partial t} + \frac{\partial J_s}{\partial Z} + \mu C_T = 0 \tag{5.3}$$

where J_s is the solute mass flow (upward) per soil area per time (g/m^2-s), C_T is the mass of solute per soil volume (g/m^3), μ is the first order degradation rate constant (per day), t is time (day), and Z is soil depth (m).

Ignoring adsorbed phase transport and hydrodynamic dispersion, the mass flux was written as

$$J_s = -D_G\left(\frac{\partial C_G}{\partial Z}\right) - D_L\left(\frac{\partial C_L}{\partial Z}\right) + J_W C_L \tag{5.4}$$

Where the first term represents gaseous diffusion, the second term describes liquid diffusion, and the third term describes convection of solute by mass flow of a soil solution. D_G and D_L represent the effective gaseous and liquid diffusivities, respectively. Hydrodynamic dispersion due to water velocity variations was neglected because average water fluxes were assumed negligible in uniform soils. Using partition coefficients for the solid, liquid, and gaseous phases and the assumption of linear, equilibrium partitioning, Equations 5.3 and 5.4 were rewritten in terms of the total concentration:

$$J_s = -D_E\left(\frac{\partial C_T}{\partial Z}\right) + V_E C_T \tag{5.5}$$

and

$$\frac{\partial C_T}{\partial t} = D_E\left(\frac{\partial^2 C_T}{\partial Z^2}\right) - V_E\left(\frac{\partial C_T}{\partial Z}\right) - \mu C_T \qquad (5.6)$$

where D_E is the effective diffusion coefficient and V_E is the effective solute convection velocity.

The following boundary conditions were identified:
$C_T(Z,0) = 0$ if $0<Z<L$,
$C_T(Z,0) = 0$ if $Z>L$,
$C_T(Z,0) = C_o$ if $L<Z<L+W$,
$C_T(\infty,t) = 0$, and
$C_T(L+W,t) = 0$.

Applying these boundary conditions and Fick's Law for the gas flux across the stagnant boundary layer, Equations 5.5 and 5.6 were successively and analytically solved to provide expressions relating the total concentration and the volatilization flux to the relevant parameters. The relevant parameters in the full Jury model included complex terms such as effective water velocity, water evaporation, a boundary transfer coefficient (H_E, m/s), and complementary error functions. However, as shown by Jury et al. (1984a), compounds with large Henry's constant (K_H) were insensitive to the thickness of the boundary layer. Therefore, a simplified solution to the model with H_E approaching infinity adequately described the behaviour of compounds with large Henry's constant. The model was further simplified by assuming zero water evaporation. The simplified model parameters included initial concentration, degradation rate, effective diffusivity, depth of contaminated layer, and depth of covering layer.

5.2.1.4 Odour emission rate model

Liao et al. (1998, 2000) used the Jury model with a decaying source strength and variable manure thickness layer to model VOC (p-cresol, toluene, xylene) volatilization from stored pig slurry. The model assumed that pig slurry was undisturbed and the components were released from the slurry layer, transported through a "clean" manure layer (assumed to have the same properties as water) as well as a manure-air interface boundary. The model simulated time-dependent volatilization, the depletion of source contaminant via both volatilization and

degradation, and could be used with a contaminated zone of finite thickness. Previously, Liao et al. (1997) published a diffusion transport model that utilized a steady-state approach which did not account for source depletion via volatilization and the stratified characteristics in the manure pit due to solids settling could also not be shown.

Liang and Liao (2004) used the complex form of the Jury model (where convective velocity was not negligible and the boundary transfer coefficient did not approach infinity) to develop a VOC-odour transport model. The model was used to develop a multiple airflow regions gamma model to characterize the extent of mixing and predicted mixing heterogeneity in a ventilated livestock building (Liang and Liao, 2004). VOC-odour profiles were generated for a variety of environmental conditions.

Finally, Smith (1995) modified a Gaussian plume dispersion model to predict spatial average odour emissions from a large area source. However, this "backward calculation" approach required simultaneous point measurements of odour concentration and wind speed at a location immediately downwind of the source (Smith, 1995).

5.2.1.5 Other Models

Other models deal with VOC emissions from wastewater treatment facilities or from stored building materials. The steady-state model described by Yaghamaei and Rashidkhani (2005) deals with VOC emissions from wastewater aeration tanks and includes provisions for VOC convection, volatilization and biodegradation. Biodegradation of compounds was calculated using Monod kinetics, and the transfer of volatile compounds between a liquid phase and a gas phase (volatilization) was modeled as a quasi-equilibrium process. In order to model the volatilization process, the mass transfer constant, concentration of VOC in effluent, the equilibrium water phase concentration and the volume of the tank were required. Chern and Chou (1999) also discuss VOC emission rates from surface aerators and include a factor for emissions from a sprayed droplet in addition to emissions from a turbulent surface. Tansel and Eyma (1999) used a general mass balance approach for VOC emissions from wastewater treatment plants and focused on losses due to volatilization and biodegradation. The authors noted that volatilization depends on concentration and properties of the volatile compound,

characteristics of the liquid phase, and the surrounding gas phase conditions while biodegradation depends on structure of compound, metabolic requirements of the microbes, and site-specific environmental conditions (Tansel and Eyma, 1999).

Several other researchers reported on VOC emission models that predict emissions from stored building materials (Haghighat and Zhang, 1999; Huang and Haghighat, 2002, Cox et al., 2002). Generally, building materials are assumed to be homogeneous and the time scale of 50 hrs is considerably shorter than landfill models. The model described by Huang and Haghighat (2002) considered mass diffusion processes within the material and the mass convection and diffusion processes in the boundary layer.

5.2.2 Effective diffusivity

Other than mass flow in the soil-water phase, the two dominant transport processes for contaminants in soil are vapour and liquid diffusion (Jury et al., 1983). The diffusivities of numerous gases in air are defined in literature as D_g^a with units of area per unit time. The diffusivities of gases in liquid (D_l^w) are less well defined but are commonly assumed to be 1000 times lower than the diffusivity of the same gas in air. The diffusivity of a gas through a medium (such as soil) is defined as the effective diffusivity (D_E). This soil gas diffusion coefficient is usually equated to the air-gas diffusion coefficient (D_g^a) multiplied by a tortuosity factor to account for the reduced flow area and increased path length of diffusing gas molecules in soil. A simplistic formula presented by Kirkham and Powers (1972) presented an average tortuosity factor of 0.5 for most soils, so the effective diffusivity was equal to half the vapour diffusivity for a given gas. Other researchers have concluded that effective diffusivity of a compound is a complex function of soil type, soil conditions, water content, porosity, chemical type, and micrometeorological conditions (Karimi et al., 1988).

In general, the effective diffusivity of a volatile pollutant in soil can be calculated if vapour diffusivity of the pollutant in air, air filled porosity of covering soil, and total porosity of covering soil are known (Karimi et al., 1986, Millington and Quirk, 1961). The Millington-Quirk

tortuosity model is shown in Equation 5.7. The soil liquid diffusion coefficient D_L is set equal to the water-liquid diffusion coefficient (D_l^w) multiplied by the tortuosity factor.

$$D_E = D_g^a \frac{\varepsilon_a^{3.33}}{\varepsilon^2} \tag{5.7}$$

where D_E = effective diffusivity in material (m^2/day),

D_g^a= diffusivity of gas in air (m^2/day),

ε_a = air filled porosity (decimal), and

ε = total porosity (decimal).

Generally, effective diffusivity through a dry soil is higher than through a wet soil because diffusivity through air is higher than diffusivity through water (Karimi et al., 1988). However, Karimi et al. (1988) found that adding liquid to a porous system reduced the effective diffusivity more than what would be expected due to the reduction of gas-filled pore space. They theorized that the presence of liquid was not merely responsible for reducing porosity, but also significantly modifying the pore geometry and the length of passage of the chemical (i.e.: tortuosity). Therefore, apparent gas diffusion through a porous medium is clearly a function of both internal geometry and porosity (Karimi et al., 1988).

According to Jury et al. (1990), the effective diffusion coefficient defines the rate of mass transfer between the liquid and gas phases. Thus D_E depends on the combined mass transfer through liquid and gas boundary layers (Liao et al., 2000) and can be expressed as:

$$D_E = \frac{(\varepsilon_a{}^{3.33} D_g^a K_H) + (\theta^{3.33} D_l^w)}{\varepsilon^2 \left[(\rho_b f_{oc} K_{oc}) + \theta + (\varepsilon_a K_H)\right]} \tag{5.8}$$

where D_E = effective diffusion coefficient in material (m^2/s),

ε_a = air content (decimal),

D_g^a = diffusivity in air (m^2/s),

K_H = Henry's law constant (dimensionless, gas to aqueous ratio),

D_l^w = diffusivity in water (m^2/s),

ε = porosity (decimal),

ρ_b = bulk density (kg/m^3),

f_{oc} = organic carbon (decimal),

K_{oc} = organic carbon partition coefficient (m^3/kg), and

θ = moisture content (decimal).

The assumption of homogeneous, isotropic material is required to apply this more complex expression for D_E.

The diffusivities of specific odour compounds (p-cresol, toluene, p-xylene) in air were summarized in Liang and Liao (2004) along with Henry's constant, organic carbon partition coefficients and degradation rates. Those values are summarized in Table 5.1.

Table 5.1. Summary of characteristics of odour components (Liang and Liao, 2004).

	D_g^a (m^2/s)	D_l^w (m^2/s)	$K_{H\,(g/aq)}$	K_{oc} (m^3/kg)	μ (d^{-1})
p-cresol	7.7×10^{-6}	7.7×10^{-10}	6.38×10^{-5}	0.047	1.034
toluene	8.8×10^{-6}	8.8×10^{-10}	0.271	0.126	3.15×10^{-2}
p-xylene	7.1×10^{-6}	7.1×10^{-10}	0.201	0.126	2.48×10^{-2}
Odour (avg)	7.87×10^{-6}	7.87×10^{-10}	0.1573	0.099667	0.3634

5.2.3 Summary

This review of previous work on the modeling of emission rates for odours and VOCs allows for the identification of guidelines related to the modeling of dour emissions resulting from the land application of manure:

- Such models must account for the volatilization of odour compounds in the short term (less than 48 hours), the degradation of odour compounds, and, in the case of injected or soil-incorporated manure, diffusion of odour compounds through the soil.
- Losses of odour compounds via other pathways (e.g. leaching, horizontal movement, etc.), convective transport, and changes in micrometeorological conditions during the modeling period may be assumed negligible.

5.3 Materials and Methods

On the basis of the guidelines presented in Section 5.2.3 above and of their simple interpretation, the Jury model was selected as a starting point to develop an odour emission rate model for the purposes of this study.

5.3.1 Jury model

As discussed in Section 5.2.1.3, a simplified version of the Jury model has been used for compounds with large Henry's constant and zero water evaporation. The Henry's constant (K_H) value for odour was estimated to be 0.1573 (dimensionless, gas to aqueous ratio) in Liang and Liao (2004), which was the average of the K_H values for three of the main odour components (p-cresol, toluene, xylene—refer to Table 5.1). According to Jiang and Kaye (1996), volatilization of compounds with a K_H value greater than 0.1009 are considered to be liquid phase controlled. Therefore, odour is also considered to have a large K_H and the solution to the model for large K_H where H_E approaches infinity adequately described the behaviour of odour. Since odours from manure application occurred in the short term for static micrometeorological conditions, water evaporation was assumed negligible. For the case of zero water evaporation ($V_E = 0$) and zero boundary layer thickness ($H_E \rightarrow$ infinity), the Jury model describing volatilization of compounds from a surface becomes:

$$J_s = C_o e^{-\mu t}\left(\frac{D_E}{\pi t}\right)^{0.5}\left[1-\exp\left(\frac{-W^2}{4D_E t}\right)\right] \qquad (5.9)$$

and the volatilization flux from a buried layer of manure located initially between z = L and z = L+W was:

$$J_s = C_o e^{-\mu t}\left(\frac{D_E}{\pi t}\right)^{0.5}\left[\exp\left(\frac{-L^2}{4D_E t}\right)-\exp\left(\frac{-(L+W)^2}{4D_E t}\right)\right] \qquad (5.10)$$

where J_s = odour flux (OU/m^2-s),

C_o = initial odour concentration (OU/m^3),

μ = first order degradation rate constant (d^{-1}),

W = thickness of contaminated material (m),

L = thickness of covering material (m),

D_E = effective diffusion coefficient of odour in slurry (m^2/s), and

t = time (days).

Note that as the covering layer thickness (L) approaches zero, Equation 5.10 approaches Equation 5.9. The assumptions required for this model included:

- the contaminant resides in three phases: an adsorbed phase, a dissolved phase, and a gaseous phase,
- the adsorbed and dissolved phases undergo reversible, linear equilibrium adsorption,
- the dissolved and gaseous phases are in equilibrium in accordance with Henry's law,
- the contaminant undergoes first-order biological/chemical degradation,
- the contaminant moves in one dimension through the medium in accordance with the principle of mass balance,
- the soil properties (total porosity, gas-filled porosity, water content, bulk density, organic carbon fraction, temperature) are constant in space and time (required to apply Equation 5.8 for D_E),
- the water flux (convective mass transfer) is negligible or significantly lower than volatilization flux,
- hydrodynamic dispersion can be ignored,
- the contaminant layer is uniform with thickness W at t=0,
- the vapour phase of contaminants diffuse up through an initially uncontaminated layer of thickness L and a stagnant air boundary layer of thickness d,
- the concentration of the contaminant above boundary layer thickness is negligible, and
- the contaminant does not exist below contaminated layer.

5.3.2 Model inputs

5.3.2.1 Initial odour concentration (C_o)

The effect of manure type, application method, and application rate on initial odour concentration was determined from the experimental data discussed in Chapter 3. Since placing the manure under the soil does not change the chemical characteristics of the manure, the initial odour concentration was the same for surface and subsurface applied manures. However, the initial odour concentration was influenced by manure type. Based on those results, the average initial odour concentration for liquid manure was 700 OU/m^3 and the average initial odour concentration for solid manure was 400 OU/m^3. Even though those concentration values were collected 20 minutes after application, they were used to represent the initial concentration at time zero (C_o) in this preliminary model. Since application rate (1X, 2X, 3X) did not significantly affect odour concentration, the C_o value did not change with application rate in the model.

5.3.2.2 First order degradation rate constant (μ)

The first order degradation rate constant was related to the half life of the compound of interest according to Equation 5.2. The first order degradation rate constant for odour in air was estimated by Liang and Liao (2004) to be 0.3634 day^{-1} which represents a half life of 1.91 days. Liao et al. (2000) reported a degradation rate of 0.0315 day^{-1} (half life of 22 days) for dust-borne odour in swine barns. However, the degradation rate constant is theoretically dependent on manure type and application method due to the physical behaviour of manure, chemical composition, and potential for rapid microbial degradation. Since liquid manure infiltrated into the soil quickly while solid manure stayed on the surface, the half life of solid manure was assumed to be longer than liquid manure. Furthermore, the manure placement was assumed to impact the degradation rate constant, particularly for solid manure. Manure placed under the soil surface theoretically had a shorter half life than manure placed on the surface due to rapid microbial activity and consumption of the volatile organic compounds in the manure. A summary of degradation rate constants used in this simulation is shown in Table 5.2.

Table 5.2. Summary of degradation rate constants (μ) used in odour emission rate simulation.

	Surface		Subsurface	
	Degradation rate (day^{-1})	Half life (day)	Degradation rate (day^{-1})	Half life (day)
Solid	0.0315	22	0.166	4.2
Liquid	0.363	1.91	0.363	1.91

5.3.2.3 Thickness of contaminated material (W)

The thickness of the contaminated material (W) depended on the application rate and application method. Obviously, the application rate dictated the volume of manure placed on or in the soil and thus, the thickness of the manure layer. Since subsurface application of manure required application in narrower bands, the manure thickness was higher for injected manure than surface applied manure at the same rate. The effective application area was approximately half for injection, so the W values were doubled for subsurface applications. Theoretically, the manure thickness will change with time for liquid manure as it infiltrates into the soil, but at this stage of model development, W was held constant. This infiltration effect was instead handled by altering the degradation rate constant for liquid manure.

The W values were estimated from the application rates used in the experimental plots in 2007, shown again in Table 5.3. Dividing the liquid rates (m^3/ha) by the 10,000 m^2/ha conversion factor converted the rate units to a thickness unit (m). Similarly, the solid application rates (Mg/ha) were converted to a length by dividing by an average bulk density (500 kg/m^3) and multiplying by the same conversion factor. The W values used in this simulation are outlined in Table 5.4.

Table 5.3. Application rates for liquid and solid manure used in experimental plots and simulations.

	Liquid (m^3/ha)	Solid (Mg/ha)
1X	56	20
2X	85	40
3X	112	60

Table 5.4. Summary of contaminated material thicknesses (W) used in simulations.

	W for liquid manure (m)		W for solid manure (m)	
Application rate	Surface	Subsurface	Surface	Subsurface
1X	0.0056	0.01	0.0055	0.01
2X	0.0084	0.016	0.009	0.018
3X	0.0112	0.022	0.012	0.024

5.3.2.4 Thickness of covering material (L)

The thickness of the covering material depended on injection depth. Theoretically, this value could range from 0 (for surface application) to infinity. The average injection depth for both liquid and solid manure was 0.075 m (7.5 cm) during the experimental data collection. To model the effect of injection depth on odour emission rate, the value of the thickness of covering material was varied from 0 to 0.2 m during the simulation.

5.3.2.5 Time (t)

Time (t) was the time after application. Odours generally return to background levels within 24 hrs of application (Hanna et al., 2000; Misselbrook et al., 1997), so the modeling period was limited to two days. Since the Jury model was invalid at t = 0, the first time step was set to 20 min (0.33 hr) to match the timing of the experimental data collected in the field. Time steps of 10 min (0.167 hr) were used thereafter to a maximum time of 2880 min (48 hr).

5.3.2.6 Effective diffusivity (D_E)

For surface applied solid manure, D_E referred to the diffusivity of odour in solid manure. For surface applied liquid manure, D_E referred to the diffusivity of odour in manure-amended soil. For injected solid and liquid manure, D_E referred to the diffusivity of odour in the covering soil. The complex model for determining D_E proposed by Jury et al. (Equation 5.8) was initially expected to more accurately assess this important property during simulations. However, for manure amended soil, the assumption of homogeneous and isotropic soil properties was not valid. Therefore, the Millington-Quirk model (Equation 5.7) was used in this study to estimate D_E values based on approximate air filled porosity and total porosity. Total porosity was estimated from the soil textural class (sandy soil porosity ranges from 0.43 and 0.36 and clayey soil porosity ranges from 0.58 and 0.51 (Buol et al., 2003)). The air-filled porosity was estimated to be the total porosity minus the volumetric water content.

As the manure infiltrated into the soil, the air filled porosity (and thus, D_E) theoretically changed. Therefore, D_E was a function of time based on the loosely approximated initial air filled porosity of the soil. Theoretically, the starting air filled porosity (and thus, D_E) also depended on manure

type and application method. In the first few hours after application, the D_E value increased (as the manure drained) based on the power law to a maximum value, then it remained constant for the remainder of the modeling period. The initial D_E value depended on only manure type for surface applied manure, but it depended on manure type and injection depth for subsurface applied manures. Expressions relating D_E as a function of time (t) and injection depth (L) are outlined in Table 5.5.

Table 5.5. Expressions for D_E (m^2/hr) as a function of time (t, hr) and injection depth (L, m) used in simulations.

Liquid surface		$D_E = 4x10^{-7}t^{3.21}$	$t \leq 12.6$ hr
		$D_E = 1.53x10^{-3}$	$t > 12.6$ hr
Solid surface		$D_E = 1x10^{-7}t^{2.95}$	$t \leq 32.8$ hr
		$D_E = 3.75x10^{-3}$	$t > 32.8$ hr
Liquid injected	$L \geq 0.06$ m	$D_E = 2x10^{-5}t^{1.59}$	$t \leq 8.7$ hr
		$D_E = 1x10^{-3}$	$t > 8.7$ hr
	$L < 0.06$ m	$D_E = 7.87x10^{-2}[0.9L+0.01+0.024t]^{3.33}$	$t \leq 8.7$ hr
		$D_E = 7.87x10^{-2}[0.9L+0.2178]^{3.33}$	$t > 8.7$ hr
Solid injected	$L \geq 0.1$ m	$D_E = 2x10^{-8}t^{3.51}$	$t \leq 32.8$ hr
		$D_E = 3.47x10^{-3}$	$t > 32.8$ hr
	$L < 0.1$ m	$D_E = 7.87x10^{-2}[-0.09L+0.011+0.012t]^{3.33}$	$t \leq 32.8$ hr
		$D_E = 7.87x10^{-2}[-0.09L+0.4046]$	$t > 32.8$ hr

For comparison, the D_E values of odour in a soil with porosity of 60% and a variety of water contents are listed in Table 5.6.

Table 5.6. Effective diffusivity of odour in soil (porosity = 60%) with a variety of water contents based on Millington-Quirk diffusivity model. The diffusivity of odour vapour in air is $2.83x10^{-2}$ m^2/hr.

Soil	Conditions	D_E (m^2/hr)	Note
Oven dry	$\theta = 0\%$, $\varepsilon_a = 60\%$	$1.44x10^{-2}$	
Dry	$\theta = 20\%$, $\varepsilon_a = 40\%$	$3.72x10^{-3}$	similar to maximum D_E for solid surface
Wet	$\theta = 30\%$, $\varepsilon_a = 30\%$	$1.42x10^{-3}$	similar to maximum D_E for liquid surface
Saturated	$\theta = 55\%$, $\varepsilon_a = 5\%$	$3.66x10^{-6}$	

θ = volumetric water content, ε_a = air filled porosity

5.3.2.7 Coverage factor (CF)

During the plot experiment in 2007, it was difficult to achieve perfect soil coverage during manure injection. As a result, the odour emission rate from injected manure behaved as if there was manure both on the surface and under the soil. The manure left on the surface contributed to

an odour emission immediately after application while the odour in the manure below the surface had to diffuse through the cover layer before being volatilized to the atmosphere. The amount of manure that behaved as if it were surface applied depended on the percent coverage achieved during the injection operation. To account for this, a percent coverage factor was introduced into the model. If the user entered 100% coverage, the odour emission behaved as if injected; if the user entered 0% coverage, the odour emission behaved as if surface applied. If the user entered 50% coverage, the model treated half of the manure applied as surface applied and half as injected and so forth.

5.3.3 Excel spreadsheet and simulations

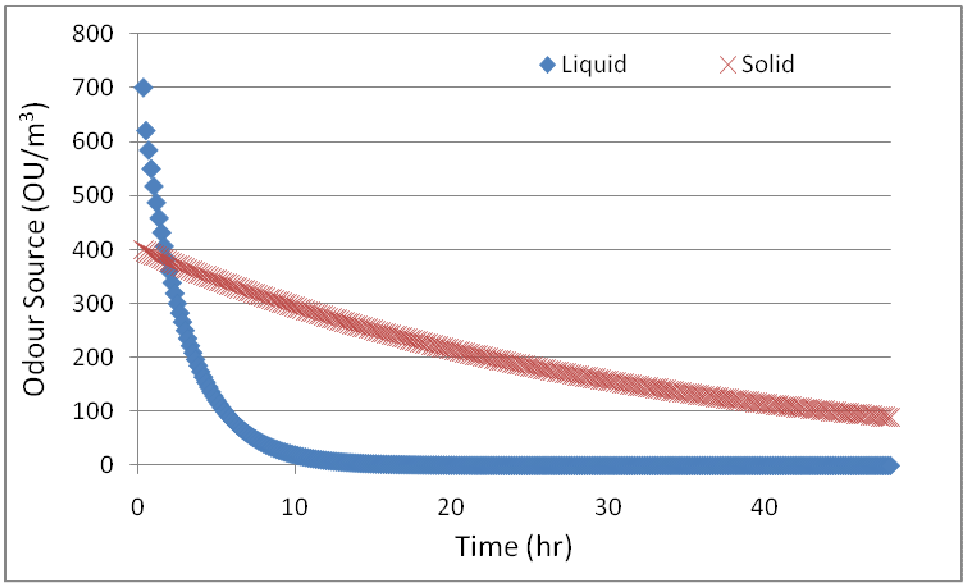
Due to its relative simplicity, the model was built as an Excel spreadsheet to calculate D_E, odour source concentration, diffusion factor, odour flux, odour emission, and cumulative odour emission for each time step. Odour source concentration was defined as the first term of the Jury model while the diffusion factor was defined as the remaining terms.

$$J_s = C_o e^{-\mu t}\left(\frac{D_E}{\pi t}\right)^{0.5}\left[\exp\left(\frac{-L^2}{4D_E t}\right) - \exp\left(\frac{-(L+W)^2}{4D_E t}\right)\right] \qquad (5.10)$$

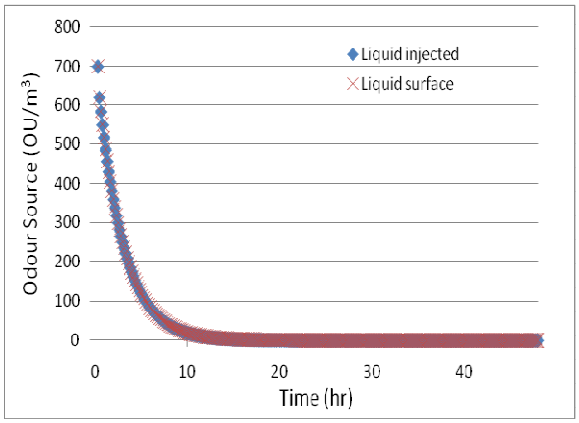
Odour source concentration — Diffusion factor

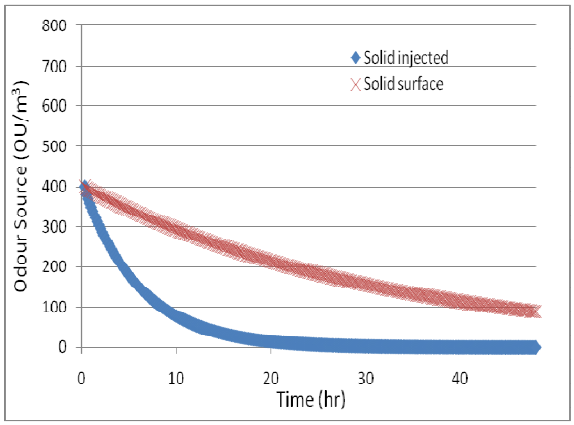
The input requirements included initial odour concentration (400 OU/m^3 for solid manure and 700 OU/m^3 for liquid manure), application rate (1X, 2X, or 3X), injection depth (0 to 0.2 m), and coverage factor (0 to 100%).

The "odour source" concentration varied with time as well as manure type and application method due to the different degradation rates defined in Table 5.2. The odour source variation with time is shown in Figure 5.1.



(a)





(b) (c)

Figure 5.1. Odour source variation with time, manure type, and application method, a) liquid vs. solid manure, b) injected vs. surface applied liquid manure, c) injected vs. surface applied solid manure.

The diffusion factor (m/hr) varied with time and was a function of injection depth, D_E, and application rate. As an illustration, the diffusion factor variation with time for surface applied solid and liquid manure applied at a 3X rate is shown in Figure 5.2.

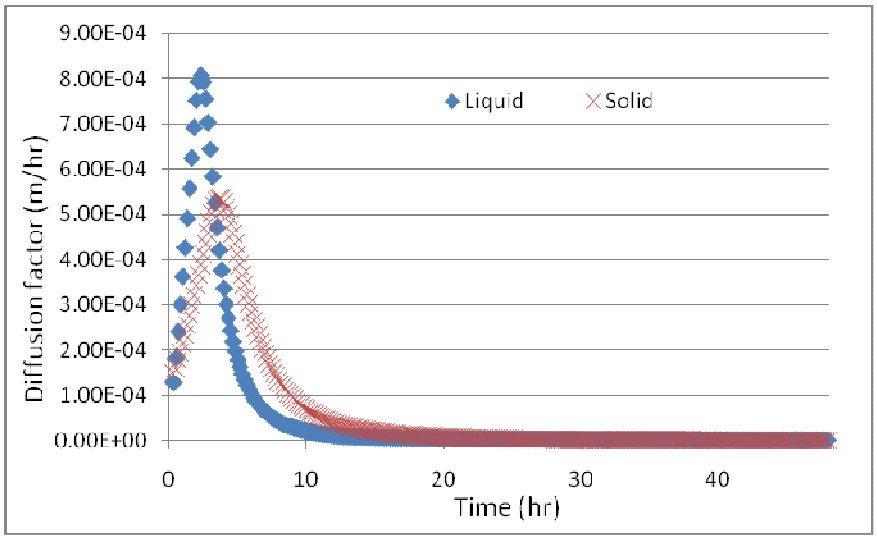


Figure 5.2. Diffusion factor variation with time for both solid and liquid manure surface applied at a 3X application rate.

Odour flux (OU/m^2-s) was defined as the product of the odour source and the diffusion factor as in Equation 5.10. In order to scale the model so that the resulting odour fluxes were in the range of the odour fluxes observed in the plot experiment (Chapter 3), a scaling factor of 80,000 was applied to both solid and liquid manure odour fluxes. This scaling factor is specific to the data collected in this study, but it does not affect the overall behaviour or trend of the modeled fluxes. Odour emissions (OU/m^2) were calculated by multiplying the odour flux by the time step (20 min (0.33 hr) for the first flux, 10 min (0.167 hr) for the remaining fluxes). Finally, the cumulative odour emission was calculated by successively summing the odour emissions.

The time to peak flux and duration of odours (length of time when the odour emission was "noticeable") were also assessed using the model outputs. To define a "noticeable" odour flux, a suitable background flux was identified. In the plot experiments, background odour emissions from the control plots averaged 0.60 OU/m^2-s or 2160 OU/m^2-hr. This translated into an odour concentration of 204 OU/m^3. However, literature stated that background odour in Tedlar bags used to collect odour samples ranged from 50 to 150 OU/m^3 (Moseley et al., 1998; Qu and Feddes, 2006). To be conservative, a concentration of 25 OU/m^3 was assumed to translate into an odour emission of approximately 250 OU/m^2-hr and, for this study, the duration of odour emissions was defined as the time the odour flux was greater than 250 OU/m^2-hr.

5.3.4 Validation data collection

In order to validate the model, additional plot data were collected in May, 2009. Since it was not possible to measure odour concentration using olfactometry at that time (the olfactometer lab was temporarily shut down), the treatment effects on odour emission trend over time were to be assessed by monitoring the p-cresol concentrations in samples collected after spreading. Since the odour volatilization model used diffusivity constants for p-cresol to represent the diffusivity of odour, measuring p-cresol concentrations was deemed appropriate for model validation.

To reliably measure p-cresol concentrations, sample air from the dynamic flux chamber (0.32 m^2, operated at 0.944 L/s, refer to Chapter 3) was drawn through sorbent tubes (XAD-7, SKC, Inc.) using a sampling pump (Airchek XR5000 Model 210-5000, SKC, Inc.). Sample air was drawn through the tube at 750 mL/min for 15 minutes to represent a sample volume of 11.25 L. For concentration measurement, the tubes were extracted with methanol and analyzed by GC/MSD. A preliminary experiment with samples collected in the dairy barn resulted in measureable p-cresol concentrations (average of 0.01 mg/m^3) using this protocol.

Using this protocol, 66 p-cresol samples were collected. Six control samples were collected (3 from undisturbed soil, 3 from disturbed soil) as well as samples from a factorial experiment with 3 repetitions:

- 2 manure types (solid, liquid)
- 2 application methods (surface, subsurface)
- 1 application rate (2X as defined in 2007 data collection)
- times after application (immediately, 30 min, 60 min, 150 min, 300 min)

Unfortunately, due to an equipment malfunction at the analysis laboratory (Saskatchewan Research Council), the samples could only be analyzed for p-cresol concentration using a GC/FID with a detection limit of 0.05 mg/m^3. None of the 66 samples registered a p-cresol concentration above the detection limit. The inability to detect p-cresol using the vented chamber and sorbent tube method may also have been due to the fact that p-cresol, with a K_H value of $6.38x10^{-5}$ (dimensionless, gas/aqueous ratio) is considered to be gas phase controlled. According

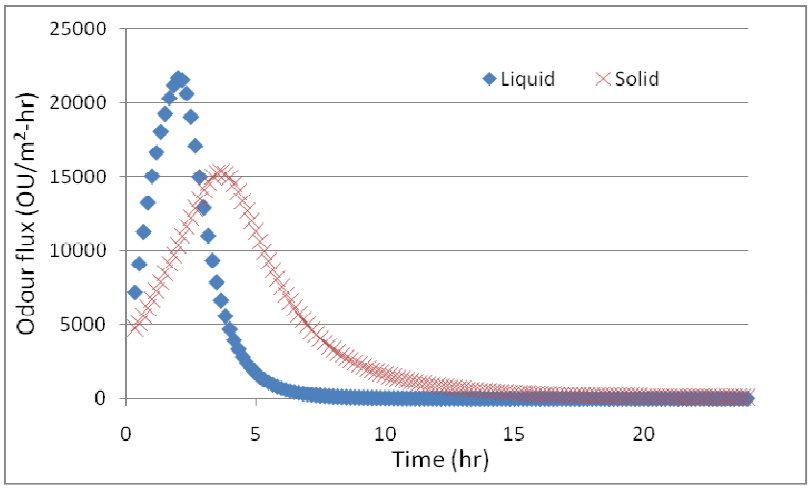
to Jiang and Kaye (1996), vented chambers are not suitable for measuring emissions of gas phase controlled substances because their volatilization is strongly influenced by wind speed, which is not well controlled with a vented chamber. Due to these measurement issues, validation of the model with experimental data was not possible for this study. General field observations were used to establish baseline values for the degradation rates and variation of D_E with time. Studies where odour was monitored over time after application (Lau et al., 2003; Misselbrook et al., 1997; Smith et al., 2007, 2008; Pain et al., 1998; Mkhabela et al., 2007, 2008) were used for a preliminary validation.

5.4 Results and Discussion

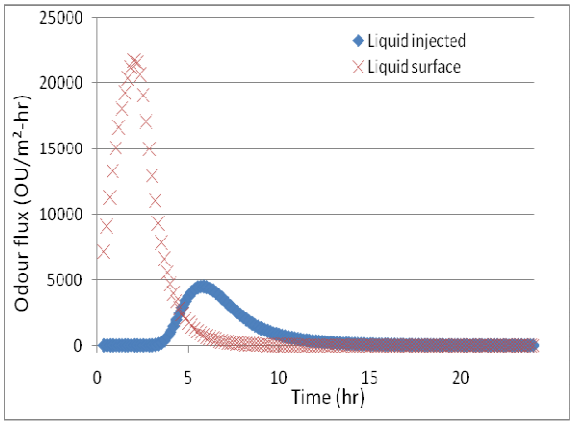
5.4.1 General model observations

The odour flux (OU/m^2-hr) variation with time showed that the odour flux reached a maximum value within three to five hours of application (Figure 5.3a). This was due to the variation in effective diffusivity with time. Initially, the low effective diffusivity of the soil inhibited odour movement, but as air spaces opened up in the topsoil, odour readily volatilized to the atmosphere. The peak flux for liquid manure was higher than the peak flux for solid manure at comparable application rates (due to a higher initial concentration value), but the odour flux from solid manure applications took longer to return to background levels (<250 OU/m^2-hr) due to a lower degradation rate (Figure 5.3a).

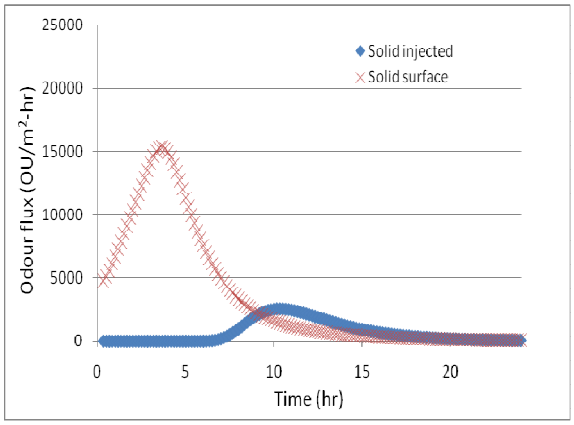
Subsurface application with 100% coverage delayed the appearance of the peak flux considerably. This was due to the time it took for the odour compounds to diffuse through the cover layer. During this time, the odour compounds underwent degradation so the peak flux was lower for subsurface applied manure than surface applied manure (Figure 5.3b and 5.3c). Subsurface application resulted in lower fluxes, but the duration of the odour event was similar to the surface application.



(a)



(b)



(c)

Figure 5.3. Odour flux simulation for a 3X application rate, a) solid vs. liquid manure, b) effect of application method for liquid manure (injection depth = 0.1 m, 100% coverage), c) effect of application method for solid manure (injection depth = 0.1 m, 100% coverage).

Even though the peak flux for solid manure was lower than for liquid manure, the longer duration of odour flux for solid manure resulted in higher cumulative odour emission (Figure 5.4). Due to the degradation of odour compounds for subsurface applied solid manure, the cumulative odour was lowest for solid manure placed beneath the soil surface (Figure 5.4).

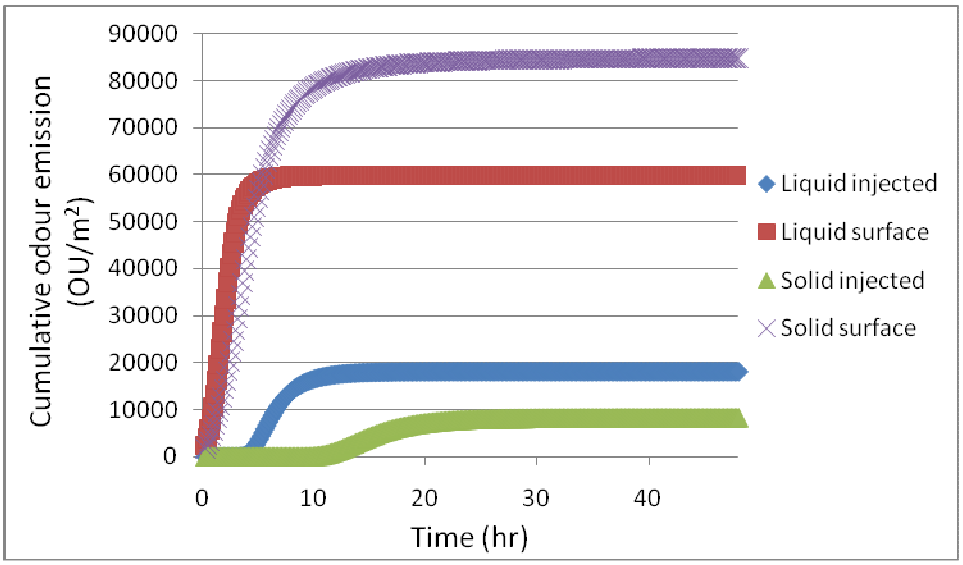
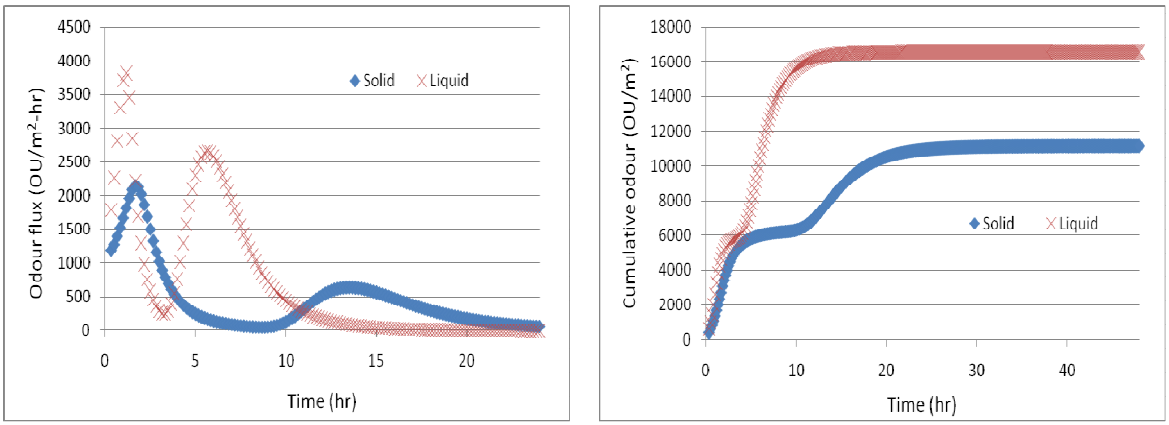


Figure 5.4. Simulated cumulative odour emissions from surface and subsurface applied liquid and solid manure applied at a 3X application rate. Injection depth was set to 0.1 m for both solid and liquid manure with 100% coverage.

Finally, when the percent coverage was less than 100% for injected manure, there were two distinct peaks on the odour flux graph (Figure 5.5a). The first peak represented the odours from the manure left on the surface while the second peak represented the odours from the manure beneath the soil surface.



(a) (b)

Figure 5.5. Odour flux (a) and cumulative odour emission (b) for injected manure with 75% coverage. Application rate was 3X, injection depth was 0.1 m.

5.4.2 Effect of manure type and application rate on odour emission trend

The results of the odour model simulation for solid and liquid surface applied manure at three application rates are shown in Table 5.7. For each manure type, the peak flux and cumulative emission increased with application rate. This was due only to the increase in thickness of the contaminated layer (W) in the model. The initial odour concentration (C_o) did not change with application rate.

Table 5.7. Effect of manure type and application rate on odour emission trend for surface applied manure.

	LIQUID			SOLID		
	1X	**2X**	**3X**	**1X**	**2X**	**3X**
Peak flux (OU/m^2-hr)	18724	20214	21678	11010	13570	15333
Time of peak (hr)	1.5	1.7	2	2.3	3.2	3.7
Cumulative emission (OU/m^2)	38675	50257	59849	43031	66055	84791
Start time (hr)	0	0	0	0	0	0
End time (hr)	5.7	6.7	7.3	11.2	14.7	17.3
Duration	5.7	6.7	7.3	11.2	14.7	17.3

The time between application and peak flux also increased with application rate. This was presumably also due to the larger thickness of material at the higher application rates. The thicker the layer, the longer it took for all of the compounds to diffuse to the top layer and begin volatilizing to the atmosphere. The duration of the odour event also increased slightly with application rate for both manure types. The duration of odours from solid manure applications were approximately double the duration for liquid manure applications at comparable application rates.

5.4.3 Effect of application mode and application rate on odour emission trend

The effect of injection and application rate on the odour emission trend is summarized in Table 5.8 for liquid manure and Table 5.9 for solid manure. The peak fluxes for injected liquid manure were 88, 83 and 79% lower than the peak fluxes for surface applied liquid manure for the 1X, 2X and 3X application rates, respectively. Similarly, liquid injection reduced the cumulative odour

emission by 77, 73 and 70% for 1X, 2X and 3X application rate, respectively. The reduction in peak fluxes for subsurface applied solid manure were 96, 94, and 93% while the reduction in cumulative emissions were 91, 90, and 90% for the 1X, 2X, and 3X application rates, respectively. These results suggest that injection should be very effective at reducing odours from both solid and liquid manure applications. However, this simulation assumes 100% soil coverage, which is often not achieved in the field. Refer to Section 5.4.5 for a discussion on the effect of soil coverage on odour reduction.

The model results indicate that injection of liquid manure actually increases the odour event duration slightly (Table 5.8), which is counterintuitive. However, following Lin and Hildemann (1995), adsorption was assumed to be one of the mechanisms that would result in lower initial emission rates. These authors showed that, in covered landfills, adsorption reduced the emission rate but resulted in prolonged emission duration. Conversely, subsurface application of solid manure did decrease the duration of the odour event (Table 5.9), likely due to the increased degradation rate defined for subsurface applied solid manure.

Table 5.8. Effect of application mode and application rate on odour emission rate trend for liquid manure.

	LIQUID SURFACE			LIQUID SUBSURFACE		
	1X	**2X**	**3X**	**1X**	**2X**	**3X**
Peak flux (OU/m^2-hr)	18724	20569	21678	2259	3435	4480
Time of peak (hr)	1.5	1.8	2	5.7	5.7	5.8
Cumulative emission (OU/m^2)	38675	50257	59849	8957	13755	18178
Start time (hr)	0	0	0	3.7	3.7	3.7
End time (hr)	5.7	6.7	7.3	10.8	11.8	12.5
Duration	5.7	6.7	7.3	7.1	8.1	8.8

Table 5.9. Effect of application mode and application rate on odour emission rate trend for solid manure.

	SOLID SURFACE			SOLID SUBSURFACE		
	1X	**2X**	**3X**	**1X**	**2X**	**3X**
Peak flux (OU/m^2-hr)	11010	13570	15333	493	839	1073
Time of peak (hr)	2.3	3.2	3.7	13.3	13.5	13.7
Cumulative emission (OU/m^2)	43031	66055	84909	3700	6381	8251
Start time (hr)	0	0	0	11	10.5	10.5
End time (hr)	11.2	14.7	17.3	17.5	19.8	20.8
Duration	11.2	14.7	17.3	6.5	9.3	10.3

5.4.4 Effect of depth of injection on odour emission trend

The effect of injection depth (L) on the odour emission trend for an application rate of 2X is shown in Table 5.10 for liquid manure. Note that the peak flux and cumulative emissions when the injection depth was zero were actually higher than the peak flux and cumulative emissions for surface applied liquid manure at the 2X rate. This was because the values in Table 4.4 assumed subsurface application (even when injection depth was zero) in narrower bands and an effective application area of approximately half that of surface application. This meant that there was less area for volatilization in the banded application, but the contaminated layer thickness was doubled, resulting in higher flux values. A modest depth of 1 cm (0.01 m) resulted in a lower peak flux and cumulative emission than the surface application, even with the higher contaminated layer thickness. Increasing the injection depth to 20 cm (0.2 m) reduced the cumulative emission by 70% compared to the typical injection depth of 10 cm (0.1 m). In practice, if injection to 20 cm was achieved with perfect coverage, the odours would likely be negligible. By the time the odours diffused through the cover layer, the volatile components of odour may be consumed or altered by the soil microorganisms. This effect could be better captured by altering the degradation rate constant for subsurface applied liquid manure.

Table 5.10. Effect of injection depth on odour emission rate trend for liquid manure.

	LIQUID SUBSURFACE--VARYING L for 2X APPLICATION RATE					
	0 m	**0.01 m**	**0.05 m**	**0.10 m**	**0.15 m**	**0.2 m**
Peak flux (OU/m^2-hr)	22759	17517	7753	3435	1632	905
Time of peak (hr)	2.3	3.2	4.3	5.7	7	8
Cumulative emission (OU/m^2)	73152	45217	25815	13755	7290	4134
Start time (hr)	0	1.7	2.7	3.7	4.8	6
End time (hr)	8.2	9.5	11	11.8	12	11.8
Duration	8.2	7.8	8.3	8.1	7.2	5.8

The effect of injection depth (L) on the odour emission trend for an application rate of 2X is shown in Table 5.11 for solid manure. In this case, the peak flux and cumulative emissions for a depth of 0 m were slightly lower than those for the surface applied 2X solid manure. The difference was due to the lower effective application area for the subsurface application. In this case, the higher degradation rate for injected solid manure resulted in lower emissions, even though the contaminated layer thickness was higher. Again, increasing the injection depth to 20

cm (0.2 m) reduced the predicted cumulative odour emissions by almost 60% compared to a typical 10 cm depth. However, injection of solid manure is an energy-intensive operation and incorporation depths of one or five cm are more common. Based on these simulated results, placing solid manure beneath 1-cm of soil would reduce cumulative odour losses by 44% and placing it beneath 5-cm of soil would reduce cumulative odour losses by 79%.

Table 5.11. Effect of injection depth on odour emission rate trend for solid manure.

	SOLID SUBSURFACE--VARYING L for 2X APPLICATION RATE					
	0 m	**0.01 m**	**0.05 m**	**0.10 m**	**0.15 m**	**0.2 m**
Peak flux (OU/m^2-hr)	10486	7226	2076	831	464	289
Time of peak (hr)	4	5.8	10.2	13.2	15.8	17.7
Cumulative emission (OU/m^2)	62404	35094	13239	6381	3920	2624
Start time (hr)	0	3.2	7.2	10.5	13.2	16.2
End time (hr)	13.3	15.2	18.3	19.8	20.2	19.8
Duration	13.3	12	11.1	9.3	7	3.6

5.4.5 Effect of coverage factor on odour emission trend

The effects of the soil coverage factor on the odour emission trends are summarized in Table 5.12 for liquid manure and Table 5.13 for solid manure. For this simulation, the application rate was 2X and the injection depth was held constant at 10 cm (0.1 m). Theoretically, the simulation for 0% coverage should behave exactly the same as the simulation for the injection with 0 m depth because they are both essentially surface applied in bands. However, the coverage factor module was designed to treat a portion of the applied manure as strictly surface applied and the remainder as injected. So, for the 0% coverage simulation, the module treated all of the manure as if it were surface applied and generated odour emission trend data from the surface applied module.

Table 5.12. Effect of coverage factor on odour emission trend for injected liquid manure.

	LIQUID SUBSURFACE, 2X APPLICATION RATE, L = 0.1 m					
	0%	**10%**	**25%**	**50%**	**75%**	**100%**
Peak flux (OU/m^2-hr)	20569	17960	14379	8653	3490	3435
Time of peak (hr)	1.8	1.7	1.7	1.3	1	5.7
Cumulative emission (OU/m^2)	50257	42436	32269	19519	12775	13755
Start time (hr)	0	0	0	0	0	3.7
End time (hr)	6.7	6.5	7	9	10.6	11.8
Duration	6.7	6.5	7	9	10.6	8.1

Table 5.13. Effect of coverage factor on odour emission trend for injected solid manure.

	SOLID SUBSURFACE, 2X APPLICATION RATE, L = 0.1 m					
	0%	**10%**	**25%**	**50%**	**75%**	**100%**
Peak flux (OU/m^2-hr)	13570	11662	9000	5071	1918	839
Time of peak (hr)	3.2	2.8	2.7	2.2	1.5	13.5
Cumulative emission (OU/m^2)	66055	54315	39004	19744	8626	6381
Start time (hr)	0	0	0	0	0	10.5
End time (hr)	14.7	13.7	12.3	8	4.2	19.8
Duration	14.7	13.7	12.3	8	4.2	9.3

Obviously, as the coverage factor increased, the peak fluxes decreased for both solid and liquid manure. However, the cumulative odour loss for 100% coverage is actually slightly higher than for 75% coverage for liquid manure. For 75% coverage, a portion of the odour compounds volatilize immediately after application and this results in a smaller secondary peak as the compounds beneath the surface diffuse to the surface. For 100% coverage, all of the compounds are available to diffuse to the surface and volatilize. For liquid manure injection, the model results indicated that an 85% coverage factor would minimize cumulative odour losses while a coverage factor of 93% would minimize cumulative odour losses for solid manure injection. However, peak fluxes were lowest when the coverage was 100%.

A better estimate of the effect of subsurface application on reducing the odour emission rate and cumulative odours can be made if reasonable coverage factors are assumed for solid and liquid manure at various application rates. For this comparison, the coverage factors for the subsurface application of liquid manure were estimated to be 70, 45, and 20% at 1X, 2X, and 3X, respectively and 80, 65, and 50% for solid manure at 1X, 2X, and 3X, respectively. The peak flux, cumulative odour emissions, and percent reduction due to injection for liquid and solid manure at three application rates are summarized in Tables 5.14 and 5.15, respectively.

Table 5.14. Effect of subsurface application on the reduction of peak odour fluxes and cumulative odour emissions for liquid manure application at three application rates. Injection depth was assumed to be 0.10 m and coverage factor was 70, 45, and 20% for 1X, 2X, and 3X, respectively.

	1X			2X			3X		
	Surface	**Injected**	**% Diff**	**Surface**	**Injected**	**% Diff**	**Surface**	**Injected**	**% Diff**
Peak flux (OU/m^2-hr)	18724	3843	79	20569	9704	53	21678	16607	23
Cumulative emission (OU/m^2)	38675	9384	76	50257	21624	57	59849	42635	29

Table 5.15. Effect of subsurface application on the reduction of peak odour fluxes and cumulative odour emissions for solid manure application at three application rates. Injection depth was assumed to be 0.10 m and coverage factor was 80, 65, and 50% for 1X, 2X, and 3X, respectively.

	1X			2X			3X		
	Surface	**Injected**	**% Diff**	**Surface**	**Injected**	**% Diff**	**Surface**	**Injected**	**% Diff**
Peak flux (OU/m^2-hr)	11010	1191	89	13510	3060	77	15333	5711	63
Cumulative emission (OU/m^2)	43031	4562	89	66055	12106	82	84909	25441	70

Compared to the odour emission reduction due to injection discussed in Section 5.4.3 (>90% for solid manure, >70% for liquid manure), these emission reduction values are more reasonable and comparable to those found in literature. This was not unexpected as literature values were collected during actual field applications where coverage factors are typically in the 50-80% range and decrease with higher application rates.

The coverage factor had no clear effect on the duration of the odour event. Increasing the coverage from 10 to 75% actually increased the duration for liquid manure (but peak fluxes and cumulative losses were lower) while it decreased the duration for solid manure.

5.4.6 Model validation

As discussed in Section 5.3.4, no usable p-cresol (odour) data were obtained from the validation experiment. Therefore, baseline values for the degradation rates and effective diffusivities were established from a combination of literature values and field experience. Adjusting some of these values (particularly the degradation rate for surface and/or injected liquid manure) may provide more realistic results.

5.4.6.1 Validation with experimental data

The experimental data collected in 2007 (covered in Chapter 3) were used to scale the odour fluxes occurring 20 minutes after application. To allow comparison with the model results, the coverage factor achieved in the field for the subsurface plots were estimated to be 70, 45, and 20% for liquid manure at 1X, 2X, and 3X, respectively and 80, 65, and 50% for solid manure at 1X, 2X, and 3X, respectively. For this simulation, the injection depth was set to 0.075 m to coincide with the plot experiments. The comparison between the experimental fluxes and modeled fluxes at 20 min after application is shown in Table 5.16.

Table 5.16. Comparison of measured and modeled 20 min fluxes.

Treatment	Application Rate	Measured 20 min flux (OU/m^2-hr)	Coverage factor (%)	Modeled 20 min flux (OU/m^2-hr)
Liquid surface	1X	9580	-	9103
	2X	8140	-	9103
	3X	7416	-	9103
Solid surface	1X	5526	-	5102
	2X	6178	-	5102
	3X	5803	-	5102
Liquid injected	1X	4702	70	2772
	2X	7063	45	4991
	3X	8060	20	7259
Solid injected	1X	2375	80	1020
	2X	3114	65	1785
	3X	2603	50	2551

In the analysis of the experimental data collected in 2007, the application rate did not significantly affect odour emissions (refer to Chapter 3). Therefore, the initial concentration in the model did not change with application rate. The thickness of the contaminated material did increase with application rate. However, this thickness did not impact the flux until 40 to 60 min after application. Therefore, the modeled surface flux at 20 minutes was not affected by application rate. The magnitudes of the modeled surface fluxes were similar to the actual surface fluxes (due to the 80,000 scaling factor applied to the flux calculation). While the model appeared to underestimate the fluxes for subsurface applications slightly, the magnitudes were also similar. The increase in modeled emissions with application rate was due only to the decrease in coverage factor.

The experimental data showed that the initial flux from surface applied liquid manure was 24% higher than the initial flux for surface applied solid manure. The model results showed that the

odour flux from liquid manure was 44% higher than from solid manure for this same comparison. Similarly, the initial flux from the injected liquid manure was 55% higher than injected solid manure while the model results showed that odour flux from liquid manure was 64% higher.

5.4.6.2 Validation with literature values

Smith et al. (2007, 2008) used micrometeorological methods to monitor the odour emission rate trend over time after application of liquid and solid manure. Their application rates (30,000 L/ha for liquid, 30 Mg/ha for solid) corresponded to approximately 1X and 2X rates for liquid and solid manure used in this study, respectively. Cumulative odours measured over 42 hours were, on average, 940,0000 OU/m^2 for solid manure and 830,000 OU/m^2 for liquid manure. A model run of surface applied solid (2X) and liquid (1X) manure resulted in predicted cumulative odour emissions that were approximately 10 times lower than those reported in Smith et al. (2007). The model predicted odours from solid manure applications that were 41% higher than liquid manure applications, compared to 12% higher measured by Smith et al. (2007). Smith et al. (2007) also found that increasing the liquid application rate from an equivalent 1X to an equivalent 2X rate increased total emissions by approximately 25%. The model results of the current study were in quite close agreement, with cumulative odour emissions from 2X surface applied liquid manure that were 23% higher than 1X surface applied liquid manure.

Smith et al. (2007) also examined odour flux evolution with time for solid and liquid manure applied to the surface. They took odour flux measurements immediately after application and 1, 6, 24, and 48 hours after application. Their results showed the maximum flux occurred one hour after application. Liquid manure resulted in a higher peak than solid manure, but the odours from the solid manure application took longer to return to background levels, resulting in higher overall emissions from solid manure applications (Smith et al., 2007). The peak flux for liquid manure was approximately 10 OU/m^2-s (36,000 OU/m^2-hr) and 6 OU/m^2-s (21,600 OU/m^2-hr) for solid manure. In the model, simulated peak fluxes from liquid and solid manure applications were approximately 19,000 and 14,000 OU/m^2-hr, respectively for similar application rates.

Rahman et al. (2001) noted that emissions measured immediately after liquid manure injection were not influenced by application rate. The model results also show no change in odour flux immediately after application for different application rates, but the coverage factor was assumed to be 100% for all rates. At higher application rates, coverage factors tend to decrease which will result in increased fluxes immediately after application, as shown in Table 5.16. Additionally, increasing the application rate resulted in higher values for the material thickness (W), which resulted in higher cumulative odour emissions for the higher application rates.

Micrometeorological methods were used by Mkhabela et al. (2007) to monitor odour emissions over time after application of liquid manure. Fluxes were measured at 0, 2, 4, 6, 18, 24, 30, and 48 hours after slurry application. Peak fluxes appeared to occur during the 6 hour measurement, corresponding well with the modeled results. The magnitudes of the peak fluxes were 72,000 OU/m^2-hr as measured in Mkhabela et al. (2008) and 21,000 OU/m^2-hr predicted by the model at 3X liquid surface applied. Mkhabela et al. (2008) also showed that the application rate did not affect the general trend of the emission rate over time after application, but the magnitudes of the fluxes were higher for the 3X rate. Similar results were obtained in the model output, shown in Figure 5.6 for 1X and 3X rates of surface applied liquid manure.

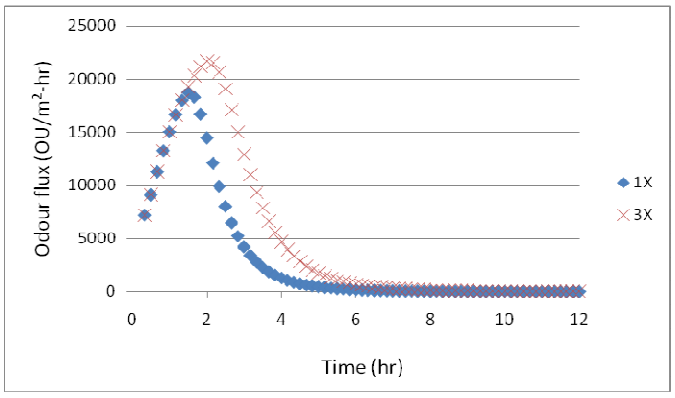
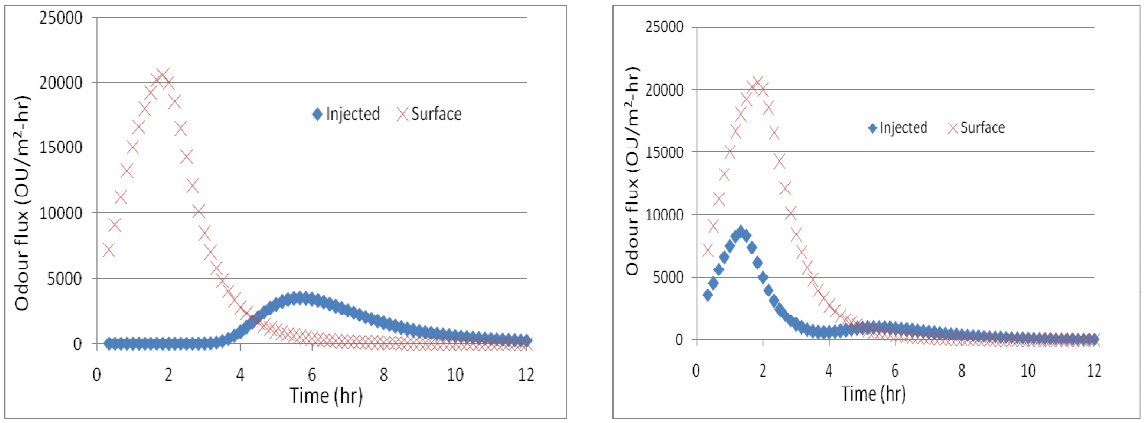


Figure 5.6. Effect of application rate on simulated odour emission rate trend over the first 12 hrs after surface application of liquid manure.

In Mkhabela et al. (2008), cumulative odour emissions from an equivalent 1X application over a 48 hour period were, on average, 1.3×10^6 OU/m^2, two orders of magnitude higher than the modeled emissions. Increasing the application rate to 2X and 3X resulted in 10 and 40% higher

cumulative losses than the 1X rate, respectively, while the model resulted in a 22 and 35% increase over the 1X rate in cumulative odour emissions.

Lau et al. (2003) used a vented chamber to monitor odour emissions after surface and subsurface application of liquid manure at an equivalent rate of 2X. Odour emissions were measured 0.5, 1.5, and 2.5 hours after application. Their highest emissions were measured at the 0.5 hour mark for both application methods and they successively decreased over time. In contrast, the model predicted that peak fluxes occurred three to five hours after application. Lau et al. (2003) noted that the odour reduction due to injection was highest at 0.5 hours after application and lessened slightly as time went by. The model results also showed that the odour reduction due to injection was greatest immediately after application. However, due to the time required to diffuse through the cover layer, the flux from subsurface applied manure was delayed significantly and occurred when the odour flux from the surface applied manure had already returned to background levels. Therefore, the model predicts odour flux from injected manure that is higher than the odour flux from the surface applied manure over a period of about 4 hours approximately 10 hours after application (Figure 5.7a). The trend of odour reduction over time observed by Lau et al. (2003) was better simulated by assuming a percent coverage of only 50% for the injected manure, as shown in Figure 5.7b. In this simulation, the maximum reduction was observed approximately one hour after application, and this reduction decreased over time. In this case, the odour flux from both the surface and injected manure returned to background at the same time, approximately five hours after application.



(a) (b)

Figure 5.7. Model predicted odour reduction over time due to injection for liquid manure application at 2X rate, a) assuming 100% coverage for injected manure, b) assuming 50% coverage for injected manure.

Other studies that have measured odour emission include those by Misselbrook et al. (1997) and Pain et al. (1991) who used micrometeorological methods to collect information on the odour emission trend over time after application of manure. However, these authors reported their results using odour concentration, which was not directly comparable to the model outputs. The data reported by these authors suggested that the peak odour concentrations occurred immediately after application and odour decreased exponentially over time over the first 10 hours after application. Local increases in odour after the 10 hour mark were attributed to increases in wind speed. The dependence of the micrometeorological calculation on wind speed may have been the reason why the modelled cumulative emissions were 10 to 100 times lower than those reported in Smith et al. (2004, 2008) and Mkhabela et al. (2007, 2008).

5.4.7 Model limitations

While most of the assumptions for the Jury model listed in Section 5.3.1 of this chapter are valid for general cases of manure application, others may lead to over- or under-estimations of odour volatilization. For example, assuming zero water velocity neglects mass transport of contaminants upward and downward, such that convective and leaching losses were assumed negligible. However, under certain conditions, prolonged upward flow of water due to evaporation and capillary rise may occur when shallow water tables are present. In such cases,

compounds that are not strongly sorbed and that have significant concentrations in the dissolved phase may have their volatilization losses enhanced when water is flowing upward and discharging at the surface (Jury et al., 1990). Therefore, for high application rates and soils with high water tables, the assumptions of zero water velocity may not be valid. However, Lin and Hildemann (1995) stated that contaminants, even those with large Henry's constant considered to be liquid phase controlled, tended to volatilize before they leached out. Therefore, leaching losses of contaminants contributing to odour are likely to be negligible.

The main limitation of the current model is the assumption of static meteorological conditions. There will be a diurnal variation in ambient and soil temperature during the 48 hour modeling period and this temperature change will alter the effective diffusivity of the soil, the main component of the model. In addition, the model assumed no rainfall during the 48 hour modeling period. Addition of water to the soil will also affect the effective diffusivity of the soil. The effect of rainfall before and after manure application was discussed in Smith et al. (2008). The authors stated that rainfall before spreading reduced the infiltration capacity of the soil, sometimes resulting in higher emission. Rainfall after spreading always reduced overall emissions because of the enhanced downward movement of contaminants (Smith et al., 2008). Mkhabela et al. (2008) also reported that fluxes were significantly dependent on weather conditions (wind speed, net radiation, evapotranspiration). While the effective diffusivity in this model is time dependent, the expressions developed in Table 5.5 were meant to capture only the change in air filled pore space as the manure first saturated the soil then drained away. Accounting for all of the effects of the changing ambient conditions on effective diffusivity would be very complex and was beyond the scope of this study.

The current version of the model does not allow for input of application rate as a continuous variable. Input of application rate is limited to discrete values of 1X, 2X, and 3X which are approximately comparable to one, two, and three year application rates. Modification of the model should allow the user to input an application rate based on total mass, volume, or nitrogen applied per hectare.

There were other minor inconsistencies in the current model, such as the results for injected manure with zero depth or 0% coverage. This particular problem may be dealt with by not allowing these extreme values to be valid for the injected module. If the injection depth or coverage factors are zero, the model should simply simulate surface application. Better estimates of μ may also result in having 100% coverage simulate the lowest cumulative odour loss (as opposed to 85% coverage for solid injection and 93% coverage for liquid injection). Other inconsistencies such as the duration of odours and presence of odour when depth is great (>0.2 m) may be solved with better estimates of the effect of manure type and application method on the degradation rate constant. Inclusion of degradation rates that reflect variable effects of soil and environmental conditions like texture and moisture would also likely improve model predictions.

5.5 Conclusions and Recommendations

A model that predicts the odour emission rate and cumulative emissions from land applied manure was developed using the mathematical model developed by Jury et al. (1990) to predict the movement of organic chemicals in soil. Modifications to the model allowed the effects of application mode (surface vs. subsurface), manure type (liquid vs. solid) on odour emissions to be simulated. The effects of injection depth and a coverage factor on emissions were also simulated. Model parameters (initial concentration, degradation rate, effective diffusivity variation with time, and a scaling factor) were estimated from experimental data collected in 2007 and literature values. These parameters resulted in modeled results that agreed reasonably well with literature values.

In general, peak fluxes were observed to occur between two and five hours after application. Peak fluxes from liquid manure applications were higher than those for solid manure applications, but the extended duration of odour emissions for solid manure resulted in higher cumulative losses from solid manure applications. The duration of odour emissions >250 OU/m^2-hr was also longer for solid applications than for liquid applications. While the

application rate had no effect on the initial odour flux, higher application rates resulted in higher peak fluxes, higher overall emissions, and longer odour durations for both manure types and application methods. In general, the ranking of cumulative odour emissions was: solid surface > liquid surface >> liquid injected > solid injected.

The model results showed that, for perfect 100% coverage, injection reduced peak fluxes and cumulative odours by more than 90% for solid manure and more than 80% for liquid manure. When typical coverage factors were assumed, the percent reduction in cumulative odours due to injection were approximately 75, 55, and 30% for liquid manure at 1X, 2X, and 3X application rates, respectively (Table 5.14) and 90, 80, and 70% for solid manure (Table 5.15). The model also suggested that the odour event duration was longer for subsurface application than surface application, even though the peak flux and cumulative losses were lower with injection. Finally, injection depths as low as 0.05 m (5 cm) were shown to significantly reduce odours from both liquid and solid manure applications compared to surface spreading.

The performance of this basic volatilization model in terms of odour prediction reveals that it may be possible to mathematically predict the odour emission rate trend after the land application of manure. The model provides baseline information on the impact of manure type, application method, application rate, depth of injection, and coverage factor on the odour emission trend. Further development is required to make the results more robust and practical. Future work should focus on better estimation of the first order degradation rate constant and the variation of effective diffusivity with time and soil conditions. Estimating the effect of transient weather conditions on the effective diffusivity can also help predict the effect of rainfall and temperature on odour emissions from manure spreading. These emission rate trends are essential for the application of dispersion models to optimize the minimum separation distances for manure spreading activities.

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Chapter 6

6.0 Better Prediction of Nitrous Oxide (N_2O) Emission Rate from Manure Spreading

A significant portion of anthropogenic nitrous oxide (N_2O) emissions come from the land application of fertilizers and manure (Mosier et al., 1996. Although N_2O is naturally produced in soils, manure management practices such as slurry injection or solid manure incorporation have the potential to influence both the short-term and long-term emissions by changing the magnitude and pattern of the nitrogen cycle in the soil-plant system. Management practices also impact the magnitude of other nitrogen losses (ammonia volatilization, nitrate leaching) which affect indirect N_2O emissions. A better understanding of the effects of application method on the short- and long-term direct and indirect N_2O emissions is required to better estimate national agricultural greenhouse gas (GHG) emissions. Results from a simple field study showed that injection increased 7-day cumulative nitrous oxide emissions from solid manure by 22 times compared to surface application. Overall carbon dioxide equivalent cumulative emissions were increased by a factor of 5 due to injection of solid manure. Collecting continuous GHG flux data from sites over several weeks or months is labour-intensive and does not always provide statistically distinguishable results. Therefore, a model that simulates the environmental conditions and nutrient transformations after manure application may allow a more convenient and reliable prediction of the effect of management practices on total GHG emissions.

Numerous process-based models have been used to estimate N_2O emissions as influenced by agricultural practices in Canada. These models simulate trace gas fluxes of carbon and nitrogen among the atmosphere, vegetation, and soil while submodels account for nitrogen gas emissions

from nitrification and denitrification. However, these models do not account for enhanced denitrification that potentially exists after slurry injection or manure incorporation, resulting in an underestimation of N_2O emissions. A simple mass balance of nitrogen after application to land shows that enhanced denitrification can increase total N_2O-N emissions by a factor of 5. By accounting for the increased microbial activity, slower oxygen diffusion and higher water filled pore space that exists after manure injection, models may better estimate N_2O emissions from manure application practices.

6.1 Introduction

Agriculture contributes to approximately 50% of the global anthropogenic nitrous oxide (N_2O) emissions (IPCC, 2001) and 72% of Canadian anthropogenic N_2O emissions (Environment Canada, 2005) (Rochette et al., 2008a). Manure and fertilizer application are the main source of agricultural N_2O emissions. The rate of N_2O production in soils is controlled by complex interactions among oxygen, nitrate, ammonium, available carbon, moisture, and temperature (Hutchinson et al., 2007). As described in Chapter 2, N_2O is produced during nutrient transformations such as nitrification and denitrification. Although N_2O is naturally produced in soils, manure management practices such as subsurface application of manure (liquid or solid) have the potential to increase both the short-term and long-term N_2O emissions by altering the nitrogen cycle in the soil-plant system. Carbon credit trading makes the magnitude and reduction of GHG emissions an important part of manure management decisions. Understanding the effect of application method on the short- and long-term N_2O emissions for both solid and liquid manure is required to better estimate the overall contribution of land application of manure to agricultural GHG emissions, and develop beneficial manure management practice (BMP) recommendations that consider impacts on GHG production along with other factors.

In addition to their impact on direct N_2O emissions, manure management techniques have an impact on the magnitude of indirect N_2O emissions. Indirect N_2O is defined as N_2O production originating from nitrogen that was emitted or transported from the source in a form other than N_2O (Del Grosso et al., 2006). For example, manure application (particularly broadcasted slurry)

results in high rates of ammonia volatilization. Volatilized N that is later deposited on soils marginally adds to the N pool in the soil. This added N increases the substrates available for nitrification and denitrification, resulting in higher N_2O emissions. Additionally, application method can influence nitrate (NO_3) leaching which can also contribute to indirect N_2O emissions (Del Grosso et al., 2006).

The impacts of manure type and application method on short-term, direct GHG fluxes were analyzed in Chapter 4. Those results clearly showed that N_2O and CO_2-e fluxes were significantly higher from liquid manure and subsurface applications. However, since measurements were made at only one time after application (24 hours), the complete impacts of manure type and application method on total emissions could not be assessed. It was hypothesized that manure type and placement would have long term effects on the GHG emissions. Loro et al. (1997) noted that solid manure application resulted in initially lower but more sustained GHG emissions than liquid manure application. This result was attributed to the organic form of nutrients present in solid manure. Organic N that was mineralized over time provided a steady supply of substrate for nutrient transformations producing N_2O. The high ammonium N content in liquid manure was rapidly nitrified to NO_3 and was either quickly used by plants or denitrified to N_2O and N_2. As a result of these phenomena, Loro et al. (1997) observed high, short bursts of N_2O fluxes immediately after application of liquid manure.

In addition to manure form, application method (surface vs. subsurface) is also expected to influence the patterns of N_2O production over time. Enhanced rapid microbial activity beneath the soil surface may produce high amounts of CO_2 and N_2O immediately after application, but rapid substrate utilization and depletion may result in lower GHG emissions from injected manure over subsequent time periods. Some studies that reported on the effect of application technique on GHG fluxes only measured fluxes one or two times after application (Lovanh et al., 2008, Sistani et al., 2008) while others continually monitored fluxes over the course of 2 to 6 weeks (Weslien et al., 1998, Perala et al., 2006, Flessa and Beese, 2000, Wulf et al., 2002). Of the studies that measured cumulative losses over a longer period, only Wulf et al. (2002) found that injection resulted in significantly higher GHG emissions on a field scale. Collecting continuous GHG flux data from sites over several weeks or months is labour-intensive and does

not always provide statistically distinguishable results. Therefore, a model that simulates the environmental conditions and nutrient transformations after manure application may allow a more reliable prediction of the effect of management practices on total GHG emissions.

The objectives of this component of the thesis research work were:

- to assess if different manure application methods impact longer-term (7 day) GHG emissions,
- to review GHG prediction models to determine if they can account for the effects of application method on total N_2O emissions from manure application,
- to estimate the magnitude of the effects of application method on total direct and indirect emissions, and
- to suggest any modifications to the models that might be required to account for these effects.

6.2 Field Assessment of Impact of Application Method on Longer-term GHG Emissions

To determine if manure type and application method have an impact on GHG emissions beyond 24 hours after application, GHG fluxes were measured daily for seven days after application of solid feedlot and liquid dairy manure. For this study, manure application was simulated by hand as described in Chapter 3 (Section 3.3.4.2). Fluxes were measured using static chambers and the same methodology used in the 2007 experiment (Chapter 4, Section 4.3.1.1) between May 20 and 29, 2009 at the U of S feedlot. The sandy loam soil properties are outlined in Table 4.7 in Chapter 4. Manure samples from this experiment were not analyzed but were obtained from the same sources as the 2007 experiment. The effects of manure type, application method, and time after application on GHG fluxes were determined using a factorial experiment with 3 replications including:

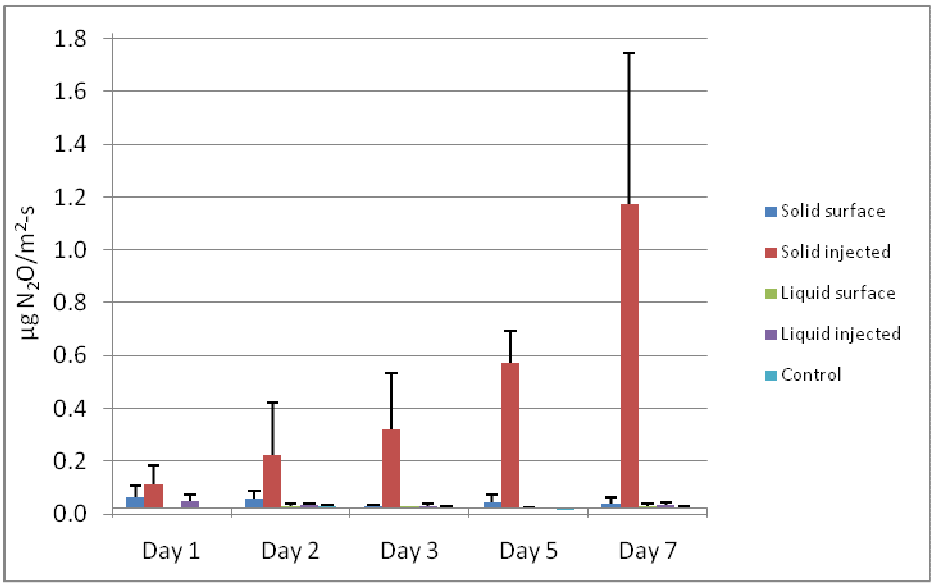
- 2 manure types (solid feedlot, liquid dairy)
- 2 application methods (surface, subsurface)

- 1 application rate (2X as defined in Table 4.4 of Chapter 4)
- 5 times after application (1 day, 2 days, 3 days, 5 days, 7 days)

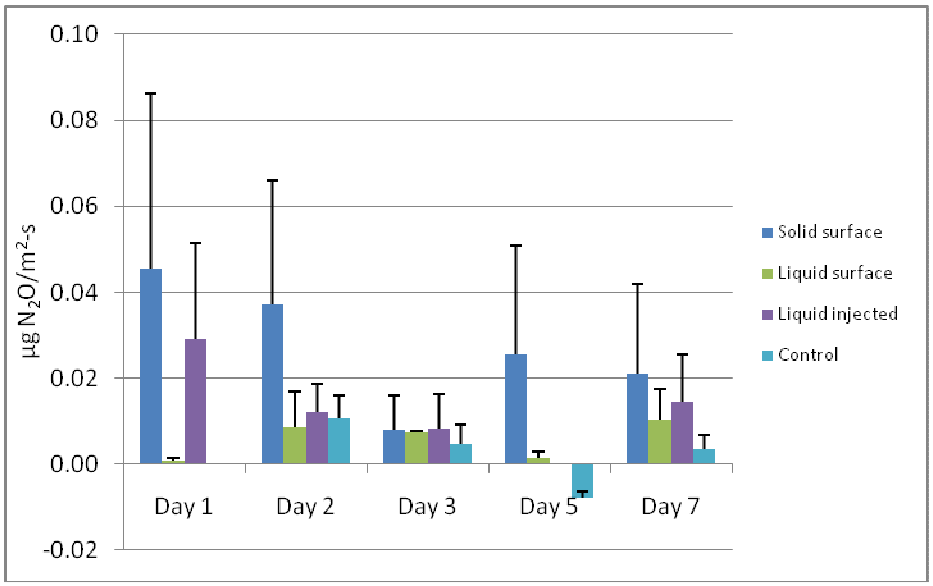
Disturbed and undisturbed control flux samples were also collected on each sampling day. Analysis of the GHG flux data over time showed highly variable fluxes for most treatments over the sampling period (7 days). The solid manure injected plots saw a surprisingly steady increase in N_2O fluxes over the sampling period (Figure 6.1a). Figure 6.1b shows the N_2O flux trend over time for all treatments except solid injected (different y-axis scale). Most of the treatments (except solid injected) were indistinguishable from each other (and in some cases, the control) for each measurement day, but there was a general decreasing trend with time.

The CO_2 flux was highly variable and most treatments were indistinguishable from each other on most days (Figure 6.2). Unlike the N_2O flux, the CO_2 flux remained relatively constant with time. Due to the high N_2O flux from the solid injected treatment, the overall CO_2-e flux has a trend similar to the N_2O flux trend (Figure 6.3).

Overall data showed that fluxes from the injected plots were higher than fluxes from the surface plots, but unlike the 2007 data, the fluxes from the solid manure were higher than fluxes from the liquid manure. It was likely that the solid manure collected from the beef feedlot was fresher for this experiment than in 2007. The total carbon and inorganic N contents are higher in fresh manure than in stockpiled or composted manure (Larney et al., 2006) which would affect the gas production rates, particularly denitrification in anaerobic zones under the soil. The fact that even the surface applied solid manure had relatively high N_2O fluxes (Figure 6.1b) agrees with the theory that the manure had higher levels of available N and C than in the 2007 experiment. However, high C:N ratios (as in the solid manure) and longer oxygen diffusion paths (as with the injected manure) usually result in complete denitrification and emission of N_2 rather than N_2O. Nonetheless, the solid manure injected treatment saw a significant emission of N_2O over the seven day sampling period.



(a)



(b)

Figure 6.1. N_2O flux trend over seven days after application (a) all treatments, (b) all treatments except solid injected. Error bars represent the standard error of the mean (positive error only—negative error bar is symmetric).

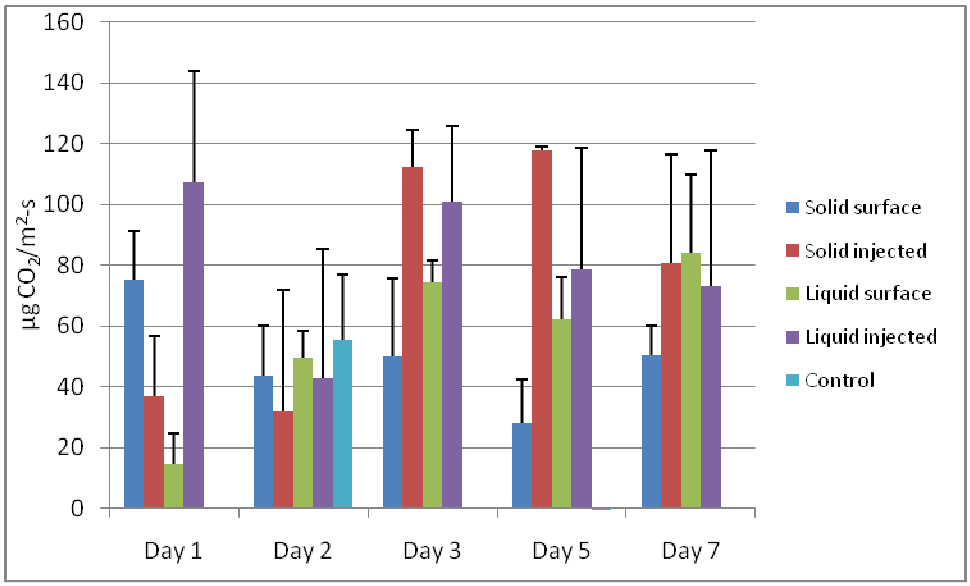


Figure 6.2. CO_2 flux trend over seven days after application. Error bars represent the standard error of the mean (positive error only—negative error bar is symmetric).

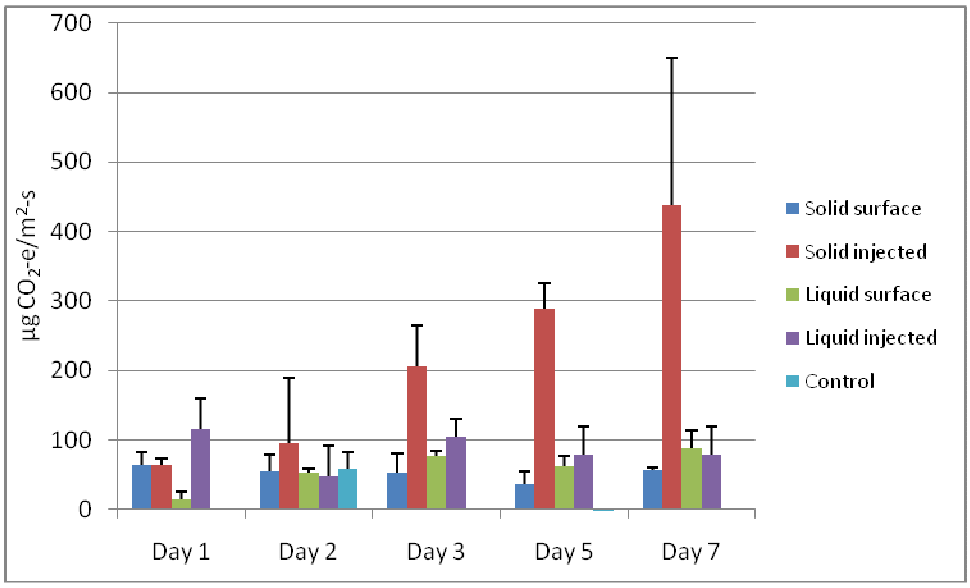


Figure 6.3. CO_2-e flux trend over seven days after application. Error bars represent the standard error of the mean (positive error only—negative error bar is symmetric).

The seven day cumulative losses of N_2O and CO_2-e were calculated by assuming that the fluxes measured on each day were constant for the 24 or 48 hours before the next flux measurement. Those results are shown in Table 6.1 for each treatment. Injection increased N_2O emissions by

22 times for solid manure and doubled N_2O emissions for liquid manure. Injection increased the overall CO_2-e emissions by 5 times for solid manure and 1.3 times for liquid manure.

Table 6.1 Estimated seven day cumulative emissions of N_2O and CO_2-e for surface and subsurface application of liquid and solid manure.

	Cumulative emission	
	(mg N_2O/ha)	(g CO_2-e/ha)
Solid surface	158	309
Solid injected	3461	1572
Liquid surface	35	383
Liquid injected	68	501
Control	6	51

One explanation for the significant increase in N_2O flux from the solid injected plots could be the fact that the solid manure is immobile beneath the soil surface. If anaerobic or partially anaerobic zones develop, they are likely to remain so until the available N is transformed, typically to N_2O and N_2 via denitrification. Injected liquid manure generates high fluxes of N_2O for a short period (as shown in previous results and in Figure 3b for day 1), but as the liquid manure infiltrates and drains from the top soil zone relatively quickly, the water filled pore space decreases, resulting in steady or declining N_2O fluxes over time (Figure 3b for days 2 to 7).

The results in Chapter 4 indicated that the manure application method influenced short-term (within 24 hours) GHG emissions while the results of this seven day study showed that application method also influenced longer-term (within 7 days) emissions. In fact, injection of solid manure appeared to dramatically increase N_2O emissions compared to surface application for at least seven days after application. If solid manure is injected during a period when there is no plant uptake (as in this study), more of the added N is likely to contribute to N_2O production since uptake of ammonium N by plants reduces the amount of ammonium left behind in the soil that can be nitrified to nitrate and subsequently be denitrified. Since the organic nutrients in solid manure mineralize over time, denitrification and N_2O emissions could occur over an extended period of time. Extended emissions of N_2O after subsurface application could be a significant factor in the overall impact of application method on GHG emissions.

6.3 Review of Greenhouse Gas Prediction Models

Since GHG emissions became a global environmental concern in the early 1990's, much effort has been spent on developing models that estimate regional and national GHG inventories. These models have evolved from simple, single factor empirical relationships to complex, process-based models that account for all of the environmental conditions that influence GHG production and emission. Several of these methodologies and models are summarized in the following sections, with focus on how they treat emissions from manure applications.

6.3.1 IPCC methodology

Since its inception in 1988, The Intergovernmental Panel on Climate Change (IPCC) has been developing methodologies for estimating carbon and nitrogen fluxes for regional and national inventories. Agricultural N_2O emissions are assumed to be derived from three principle sources: 1) direct emissions from soil N, 2) emissions from animal waste management systems, and 3) indirect emissions from N lost to the agricultural system through leaching, runoff, or atmospheric deposition. Each source has at least one emission factor (EF), which estimates the proportion of the total N input that is emitted as N_2O. Emission factors have a defined default value and a specified range, derived by IPCC from published information. The IPCC emission factors are essentially production based and do not account for climate, land use management practices, soil types, and other controlling variables. The advantages of the IPCC methodology are its simplicity, global coverage, transparency, and use of readily available information (Hutchinson et al., 2007).

Of the three main sources of agricultural N_2O emissions, land application of manure contributes to 1) and 3). The current IPCC methodology for predicting N_2O from agricultural land assumes a default EF of 1.25% (IPCC 1997) or 1% (IPCC 2006) of all N added to the soil (Chen et al., 2008). While 1.25 or 1% of unvolatilized N inputs are lost from soil as direct N_2O emission, approximately 10% of synthetic fertilizer N and 20% of organic fertilizer N applied is assumed to be volatilized (Del Grosso et al., 2006), regardless of application method. Furthermore, 30%

of applied N is assumed to leach or run off into the groundwater or surface waters (Del Grosso et al., 2006). Indirect N_2O emission is the sum of 1% of the volatilized gases (NH_3) and 2.5% (IPCC 1997) or 0.75% (IPCC 2006) of the nitrate leached to surface or ground waters (Del Grosso et al., 2006). Therefore, in this approach to N_2O prediction, manure placement does not affect total N_2O emissions.

This Tier I IPCC approach does not account for regional differences in agroecosystem characteristics (Hutchinson et al., 2007). Yet, we know that important differences exist across the country in the interactions between climate, soil properties, crop type, fertilizer use, and agricultural management that can lead to marked differences in N_2O emission patterns at the national scale (Li et al., 1996 in: Hutchinson et al., 2007). A Tier II methodology for estimating the N_2O emissions from agricultural soils was developed according to the main framework proposed by IPCC (1997) in Hutchinson et al. (2007). It accounted for the sources identified by the Tier I approach such as the stimulation of N_2O production by the addition of N as synthetic fertilizers, animal manure, crop residues and mineralization of native soil organic matter. The Tier II approach proposed the following changes:

1. Emissions are calculated at a regional scale to take advantage of activity data that are available at small spatial scales and to account for the influence of local conditions on soil N_2O dynamics,
2. A spatially and temporally variable emission factor based on climate moisture regime replaces the Tier I EF (1 to 1.25% of applied N),
3. The influence of several management practices (soil tillage, summer fallow and irrigation) is added,
4. The contribution of emissions during winter and spring thaw are included,
5. The impact of landscape position on N_2O emissions is accounted for,
6. The influence of soil texture is added, and
7. The contribution of biological N fixation is omitted based on the findings of Rochette and Janzen (2005) that the contribution of biological N fixation to N_2O emissions are negligible.

Rochette et al. (2008b) noted that different Canadian regions required the application of different EF's for direct emissions, as indicated by the second item in the list above. The relatively low N_2O emissions in the Canadian Prairies compared to Eastern Canada were attributed to the fact that N_2O production in the Prairies is often not limited by mineral N availability, but by other factors, including low denitrification activity under the well-aerated soil conditions in the semi-arid environment of the Prairies (Rochette et al., 2008b). Therefore, lower fertilizer induced emission factors should be applied in the dry Prairie region (Rochette et al., 2008b).

The IPCC methodology also does not account for the effect of less frequent applications of manure at higher rates. In areas where over-application of nutrients is not a concern, producers can apply manure at triple the recommended rate every three years rather than applying the recommended rate every year to reduce costs and compaction. Emission factors from these three-year applications may be considerably different from factors for annual applications in the first year, particularly the leaching and run-off factor. In subsequent years, the emission factors for all the nutrient pathways (volatilization, leaching, run-off) will likely be lower than the first year, but higher than emission factors for bare soil due to residual and mineralized nutrients. The emission factors for multi-year applications of manure need to be established.

Nitrogen application contributes to approximately 45% of direct sources of N_2O in Canada (35% from synthetic N fertilizer and 10% from manure application) (Rochette et al., 2008b). However, estimating N_2O losses after land application of manure and fertilizers requires much guess work, and in most inventories using IPCC methodology, the application method was not a factor in the N_2O emission estimation.

6.3.2 Simplified process models

Heinen (2006) compiled a description of N_2O emission models that used readily available inputs. These simplified process models were easy to use but did not consider the complex feedback of microbial processes or gaseous diffusion. The most basic models were based on soil property or organic carbon dynamics or first order decay processes. Some of these models included denitrification as a function of nitrate, water content, temperature, pH, carbon content. Such

models were practical to use in studies where denitrification at a field scale was to be determined (Heinen, 2006).

The popular "hole in pipe" (HIP) model (Firestone and Davidson, 1989) depicted N gas fluxes as by-products of gross inorganic N fluxes, a direct result of the soil microbial activity regulated by soil environmental conditions, which in turn control 1) the nitrification and denitrification processes dictating N fluxes through the "process pipe", 2) the partitioning of N gases via the size of holes in the pipe through which NO, N_2O or N_2 leak, and 3) the diffusion of trace gas across the aqueous-air interface (Chen et al., 2008). However, the potential loss of N_2O or NO from total mineralized N was set to an empirical default value of 2%, which tended to overestimate emissions in most agro-ecosystems (Chen et al., 2008).

In various simplified process models, denitrification, nitrification, and nitrate content have all been described using Michaelis-Menten kinetics. Michaelis-Menten kinetics describe an asymptotic relationship between emission rate and substrate concentration and are used to describe the behaviour of many enzymes and microbial populations. Cumulative ammonia losses were described using Michaelis-Menten kinetics in Chapter 5. Michaelis-Menten parameters represent maximum concentration as time approaches infinity and the time at which the concentration reaches half of maximum.

For example, Müller et al. (1997) reported on a mechanistic model for N_2O emission via nitrification and denitrification (KNOM). While denitrification was modelled according to Michaelis-Menten kinetics, the N_2O via nitrification was modelled by a function of soil temperature and soil water content. The relevant Michaelis-Menten parameters of each process were estimated from soil temperature, soil water content and soil mineral N concentrations. The DAISY model was another simplified process model that adopted Michaelis-Menten kinetics to calculate nitrification rate (Wu and McGechan, 1998). Michaelis-Menten parameters ranged from 100 g N_2O-N/ha-day to 1000 g N_2O-N/ha-day depending on driving factors in Müller et al. (1997).

While none of the models that utilize Michaelis-Menten kinetics discussed the impact of N application method on the denitrification potential and subsequent N_2O production, the effect of subsurface application of N on N_2O emissions could be captured by deriving appropriate Michaelis-Menten parameters. For N_2O emissions, application method is likely to affect both the maximum value (N_{max}) as well as the time at which the concentration reaches half of maximum (K_m).

Using a different approach, nitrification of ammonium to nitrate in the SOILN model (the N submodel for the Swedish soil water and heat model SOIL) was considered to be a first-order rate process, driven by the excess of ammonium above an assumed equilibrium ammonium to nitrate ratio (Wu and McGechan, 1998). McGechan et al. (2001) used the SOILN model to investigate the effects of nitrogen management scenarios on nitrate drainage flows, total gaseous nitrogen losses, and crop yields. Slurry spreading equipment options included a vacuum tanker with a splash plate and a tanker-mounted shallow injector. Results showed that denitrification losses were more than twice as high from grassland compared with the arable cropland due to larger nitrogen pools, particularly organic nitrogen, in the grassland soil (McGechan et al., 2001). However, denitrification losses differed little between the different slurry management options (McGechan et al., 2001). This suggests that the model does not account for the enhanced denitrification that occurs after manure injection.

Single and multivariate regression analyses have produced various models that predict N_2O loss based on factors such as application rate, soil aeration, soil temperature, soil mineral-N, and land use factors (Mosier et al., 1983; Sozanska et al., 2002 and Conen et al., 2000 in: Chen et al., 2008). However, these regression models are applicable to conditions specified in the study and none of the regression models accounted for the method of application.

6.3.3 Ecosystem models

While the IPCC methodology is useful for obtaining rough estimates of national GHG emissions, it does not include any interaction or feedback between various components of the N cycle. Therefore, it is not possible to assess the potential impacts of any agricultural management other

than total N addition on emissions. Likewise, the simplified process models are limited to simulating soil N_2O production through nitrification and denitrification. However, the mechanisms responsible for and interacting with gaseous N transformation and movement in soils include adsorption, diffusion, volatilization, degradation, leaching, nitrification, denitrification, mineralization, immobilization, and plant uptake. Since fertilizer type and placement are likely to affect several of these mechanisms, a more sophisticated model is required to accurately simulate the effects of subsurface application on total GHG emissions.

There are numerous "microbial growth models" that model the dynamics of the microbial organisms responsible for the N cycling process. All of these models account for soil-air atmosphere and climate interactions, plant growth, C and N cycling, and land use management (Chen et al., 2008). In the N cycling component of each model, the contributions of N_2O from both denitrification and nitrification are estimated (Chen et al., 2008). In most of these models, the growth of the microbial biomass was calculated by a first-order kinetic equation in which their relative growth rate was described by a double Monod equation consisting of rate-limiting factors for C and N substrates (Chen et al., 2008).

Microbial growth models allow simulations of the more intricate soil processes and feedbacks within the system, and testing management changes. Several field scale process-based models exist that include modules for N transformation prediction, including the DeNitrification-DeComposition model (DNDC, Li et al., 1992a,b), DAYCENT (Del Grosso et al., 2006), and the *ecosys* model (Grant et al., 2001; 2006). These models have been used on a regional scale to predict GHG losses from agro-ecosystems and are described in Sections 6.3.3.1 to 6.3.3.3. A summary of the structure and functionality of these models (from Chen et al., 2008) is included in Table 6.2. Section 6.3.4 discusses the application of these and other models to estimate the emissions as influenced by agricultural practices.

6.3.3.1 DNDC

The DNDC model (Li, 2007a) is a computer simulation model of carbon and nitrogen biogeochemistry in agro-ecosystems. DNDC can be used for predicting crop growth, soil temperature and moisture regimes, soil carbon dynamics, nitrogen leaching, and emissions of

trace gases including N_2O, CH_4, and CO_2 (DNDC, 2007). It was specifically developed to predict daily N_2O fluxes through the nitrification and denitrification pathways, CO_2 production from decomposition of organic matter and root respiration, as well as anaerobic CH_4 production within agro-ecosystems. The DNDC model consists of two components. The first component includes soil climate, crop growth and decomposition submodels, predicts soil temperature, water content, pH fluctuation, redox potential (Eh), and substrate concentration profiles (DNDC, 2009).

The denitrification submodel of DNDC is activated when soil water content increases or when soil oxygen availability decreases due to rain, irrigation, or cold temperatures. Denitrification is simulated via the basic laws of sequential chemical kinetic reactions to calculate NO, N_2O and N_2 fluxes ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$) with a fraction of the N pool converting directly to N_2O (Chen et al., 2008). The DNDC model simulates relative growth rates of nitrate, nitrite, NO, and N_2O denitrifiers based on soil Eh, pH, dissolved organic C and N oxides. An innovative concept called "anaerobic balloon" was developed in the model to divide the soil matrix into aerobic and anaerobic parts. Only the substrates located in the anaerobic zone are engaged in the denitrification process (Chen et al., 2008). Diffusion rates of N_2O in the soil matrix are a function of soil porosity, soil water content, soil temperature, and soil clay content.

Input parameters for the DNDC model include information for eight submodels: crop, tillage, fertilization, manure amendment, weeding, flooding, irrigation, and grazing/cutting. Within the manure amendment submodel, the number and dates of manure applications, manure type (farmyard manure, green manure, straw, liquid animal waste, and compost), application rate (kg C/ha) and C/N ratio of the manure are required. While application method is not included in the manure application submodel, surface application and injection can be specified for the fertilization submodel. The DNDC documentation notes that injection is typically used for anhydrous ammonia.

6.3.3.2 DAYCENT

DAYCENT is the daily time step version of the CENTURY ecosystem model (Parton et al. 1988a, b in: Chen et al., 2008) which can simulate trace gas fluxes of NO, N_2O and N_2 from soils

as well as terrestrial CH_4 formation and oxidation. The finer time scale is used in DAYCENT because trace gas fluxes are often short term episodic events in response to rainfall, snow melt, or irrigation. DAYCENT includes submodels for land productivity, decomposition of dead plant material and soil organic matter (SOM), soil water and temperature dynamics, and trace gas fluxes. The model was designed to be linked with larger-scale nutrient cycling models (CENTURY) so that estimates of soil N gas flux through natural and managed systems can be improved (Del Grosso et al., 2000).

In the nitrification submodel, N_2O emissions are simulated as a function of soil ammonium content, soil water content, temperature, pH and soil texture (Parton et al., 1996 in: Chen et al., 2008). Nitrification is limited by moisture stress when soil water filled pore space (WFPS) is too low and by oxygen availability when WFPS is too high. N_2O emissions from nitrification are estimated using a fixed fraction of the soil nitrification rate (i.e.: 2%).

The denitrification submodel simulates N_2O and N_2 emissions as a function of soil nitrate (electron acceptor), oxygen availability (competing electron acceptor), labile C availability (electron donor), and soil physical properties related to texture that influence gas diffusion rates (Del Grosso et al., 2000 in: Chen et al., 2008). Simulated heterotrophic CO_2 respiration is used as a surrogate for labile C availability and the oxygen status of the soil is calculated as a function of WFPS, soil physical properties that control gas diffusivity, and O_2 demand (simulated heterotrophic respiration rates) (Parton et al., 2001). Denitrification is triggered when soil WFPS exceeds a texture-related threshold, and then it increases exponentially as WFPS increases and levels off as the soil approaches saturation (Del Grosso et al., 2000).

The denitrification submodel assumes that the process controlled by the molecular species or environmental conditions is the one that is most limiting. Between 55 and 90% WFPS, denitrification rates increase exponentially and the rate of increase levels off as soils approach saturation. No denitrification is assumed to occur at WFPS < 55%. The model assumes that denitrification occurs in anoxic microsites when NO_3 and C are available (Del Grosso et al. 2000).

Input data for DAYCENT includes daily weather variables (max/min air temperature, precipitation, solar radiation, relative humidity, wind speed), site-specific soil properties (such as bulk density, soil water contents at wilting point, field capacity and saturation and saturated soil hydraulic conductivity), and current and historical land use (Del Grosso et al., 2006). Outputs include daily N-gas flux (N_2O, NO_x, N_2), CH_4 uptake, CO_2 flux from heterotrophic soil respiration, actual evapotranspiration, soil NO_3, water content, and temperature by horizon, soil NH_4 in top 15 cm, H_2O and NO_3 leaching, weekly live biomass, soil organic C and N, and several other ecosystem parameters (Del Grosso et al., 2006). While DAYCENT is designed to handle N inputs in the form of fertilizer, manure application and application mode do not appear to be factors.

6.3.3.3 ecosys

In the *ecosys* model, the key biological processes (mineralization, immobilization, nitrification, denitrification, root and mycorrhizial uptake) controlling the generation of N_2O were coupled with the key physical processes (convection, diffusion, volatilization, dissolution) controlling the transport of the gaseous reactants and products of these biological processes (Grant et al., 2006). The model integrates temporal scales from seconds to centuries and is made up of seven submodels. The production of gaseous C and N products is associated with the microbial activity submodel. Microbial populations undergo first-order decomposition, the products of which are partitioned between humus and microbial residue according to a function of soil clay content.

Compared to the other models, *ecosys* has a large input data requirement: hourly or daily climate variables, site geographic information, soil properties by layers, plant characteristics and land use management. This model has been used to predict the impact of different manure management strategies on overall GHG emissions in Canada and the US. Model results in Grant et al. (2006) indicated that N_2O emissions rose non-linearly with fertilizer application rates when these rates caused mineral N availability to exceed ecosystem (crop + soil) N uptake capacity. However, there appears to be no work with *ecosys* to determine the impact of manure type and application method on total GHG emissions. Chen et al. (2008) noted that the parameterization of such an extremely comprehensive model is very difficult for inexperienced users.

Table 6.2. Structure and functionality of three field scale N_2O simulation models (adapted from Chen et al., 2008).

Model	DAYCENT	DNDC	*ecosys*
Time step	Daily	Daily	Seconds to centuries
C cycling	8 C pools	8 C pools	6 organic states, 4 organic matter-microbe complexes and 6 biological organization
N cycling*	6 processes, NH_3, NO, N_2O and N_2	6 processes, NH_3, NO, N_2O and N_2	6 processes, NH_3, N_2O and N_2
Nitrification	First-order kinetics, N_2O fixed proportion (2%)	Nitrifier dynamics, N_2O fixed proportion (0.25%)	Nitrifier dynamics, N_2O dynamic
Denitrification	Based on WFPS threshold driven and first-order kinetics	Denitrifier dynamics and "anaerobic balloon" driven	Denitrifier dynamics
Gas diffusion	Soil diffusivity based on soil texture	Diffusion proportion	Dynamic
Land use	Crops, pastures, forests	Crops, pastures, forests	Crops, pastures, forests
Applications	USA, Canada, Australia, New Zealand and Europe	USA, Australia, New Zealand, Europe, China and India	USA and Canada

*Note: all 3 of these models include the N cycling processes of mineralization, immobilization, ammonia volatilization, nitrification, denitrification and nitrate leaching.

6.3.4 Model Applications

6.3.4.1 IPCC methodology

The IPCC methodology has been extensively used to estimate national GHG inventories, but because of its lack of detail, it is difficult to use IPCC methodology to estimate the effect of management practices on GHG emissions. Recently, Rochette et al. (2008a) developed a country-specific IPCC methodology for estimating N_2O emissions from agricultural soils. Their Tier II approach was outlined in Section 3.1 and required an estimation of the regional emission factors for N inputs, spring thaw, tillage intensity, soil texture, irrigation, landscape, summer fallow, and other sources of N_2O emissions. While this approach allowed simulation of more management-specific scenarios than the Tier I methodology, it does not account for the effects of subsurface application of fertilizers and manures.

6.3.4.2 DNDC

Most studies utilizing DNDC have focused on the effect of N-fertilizer application rate, crop rotation, tillage practices, use of cover crops, and use of manure as a fertilizer on trace gas fluxes. While different application methods are available for fertilizer application (i.e.: injection of anhydrous ammonia), manure can only be surface applied. Li et al. (1996) stated that, of the agricultural practices simulated including fertilizer amount, fertilizer type, fertilizing depth, fertilizing timing, tillage, and manure content, manure additions had the most pronounced impact on N_2O emissions. The main effect of manure application is the addition of organic matter into the soil organic carbon (SOC) pool and increasing N_2O emission rates through elevating nitrate and soluble C concentrations in soils. Spreading of manure increases the C content required for denitrification, enhances soil nitrogen mineralization, and increases the efficiency of N_2O production (Li et al., 2007b). But the negative effect of increase in N_2O emission was offset by the positive effect of the increase in SOC, resulting in net C sequestration (Li, 1995).

Smith et al. (2004) utilized the DNDC model to estimate the inter-annual variations of N_2O emissions from agricultural soils in Canada. Simulations were carried out for three soil textures in seven soil groups, with two to four crop rotations within each soil group using climate data from 1970 to 1999. There was a general trend towards increasing N_2O emissions over time, attributed to an increase in N-fertilizer application and higher daily minimum temperatures. Grant et al. (2004) used the DNDC model to predict the effects of converting cultivated land to grassland, converting from conventional tillage to no-tillage, elimination of summer fallow, increasing and decreasing N application rates, and spring vs. fall applications of fertilizer on N_2O emissions. The results were sometimes region-specific (i.e.: converting to no-till has a different effect in western Canada than eastern Canada), but increasing N application rates always increased N_2O emissions.

Neufeldt et al. (2006) noted that neither economic nor ecosystem models alone can provide an integrated estimate of the economic and environmental effects of different mitigation options. Therefore, the authors coupled an economic farm emission model (EFEM) that simulated how agricultural policies and the socioeconomic frameworks influence farmer decisions on management options, with an ecosystem model (DNDC) that used the information on land-use

distribution and intensity to simulate GHG emissions as a function of climate, soil, and management specific parameters (Neufeldt et al., 2006). Coupling the models allowed evaluation of the environmental effectiveness and the economic viability of possible GHG mitigation measures at regional scales. Although manure application method was not considered a factor, this type of model would allow a full assessment of the impact of manure injection, including environmental factors like increased N_2O as well as economic implications related to carbon credits and increased energy consumption.

6.3.4.3 DNDC vs IPCC

Several studies have directly compared estimates of emissions from the DNDC model and IPCC methodology. Since DNDC only predicts direct N_2O emissions, most studies only calculated direct N_2O emissions using IPCC. Hutchinson et al. (2007) concluded that the DNDC model estimated higher direct N_2O losses than the Tier II IPCC approach for Canadian agroecosystems. Conversely, Horak and Siska (2006) showed that the DNDC simulations for N_2O emission from sandy loam soil in the Slovak republic were lower than IPCC methodology estimations (1.25% EF), but they were within the ±1% error for most years. While the authors stated that manure application and mode and timing of application showed strong inter-annual variability in emissions, these factors are not accounted for in either model. Essential data for estimating trace gas fluxes included fertilizer use, the mass of residue in the soil and the amount of crop residue produced.

IPCC and DNDC were used to estimate the effect of landscape location (shoulder, footslope, etc.) on N_2O emissions at two sites in Canada (Smith et al., 2002). The two sites provided a variety of crops, management practices, soils, and climates for testing the models. While the DNDC resulted in an underestimation of 8% for the footslope position and an overestimation of 46% for the shoulder position compared to measured fluxes, the DNDC model was more accurate than IPCC methodology at estimating N_2O emissions at both sites (Smith et al., 2002).

6.3.4.4 DAYCENT

In validation studies, the DAYCENT model was relatively simple and more empirical compared to more detailed ecosystem models (Grant and Pattey, 2003 in: Chen et al., 2008). In USA systems, it has been shown to accurately simulate mean annual N_2O emissions, however its ability to replicate daily emissions is less reliable (Del Grosso et al., 2000 in: Chen et al., 2008).

In Del Grosso et al. (2008), DAYCENT was used to estimate N_2O emissions from irrigated cropping systems in Colorado. The model overestimated N_2O emissions and underestimated NO_3 levels, particularly for treatments receiving no N fertilizer. The model results were improved by lowering the amount of N_2O emitted per unit of N nitrified from 2% to 1%, but the treatments receiving no N fertilizer were still overestimated by more than a factor of two. The authors suggested that DAYCENT could be improved by reducing the background nitrification rate and by accounting for the impact of changes in microbial community structure on denitrification rates. DAYCENT could also be improved by raising the minimum threshold of soil NH_4 required for nitrification to occur. DAYCENT simulations in Del Grosso et al. (2009) showed that precision application of fertilizer and use of nitrification inhibitors reduced gaseous N losses and NO_3 leaching by allowing for more N uptake by the plants. No-till cultivation, which facilitates C sequestration in soils, combined with nitrification inhibitors, provided the maximum reduction in GHG fluxes among the scenarios considered. Reduced fertilizer application rates reduced gaseous N losses, but yields were reduced by a similar proportion (Del Grosso et al., 2009). Manure application and application mode were not considered in any reported DAYCENT simulations.

6.3.4.5 Integrated Farm System Model (IFSM)

The Integrated Farm System Management (IFSM) model was developed by the USDA Agricultural Research Service, University Park, Pa. It is a process-level whole-farm simulation model that includes major components for soil processes, crop growth, field operations, feed storage, feeding, herd production, manure handling, and economics (Rotz et al., 2009). IFSM predicts the effect of management options on farm profitability and environmental pollutants such as nitrate leaching, ammonia volatilization, and phosphorus runoff (Chianese et al., 2009a).

The N_2O module of DAYCENT was used to predict gaseous N emissions from cropland in IFSM (Chianese et al., 2009c). Emissions of N_2O from soils were predicted by DAYCENT as the sum of nitrification and denitrification losses. The soil N cycle was already simulated in prior versions of IFSM using the Nitrate Leaching and Economic Analysis Package (NLEAP) model (Shaffer et al., 1991) so the soil nitrification rate and nitrate concentrations were available. Emission of N_2O due to denitrification was a function of the soil nitrate concentration, the soil respiration, WFPS, ratio of N_2 to N_2O emission, soil bulk density, and active soil depth. The effects of soil nitrate and CO_2 flux on denitrification were predicted by empirical equations, as described by Parton et al. (2001). In IFSM, the Millington-Quirk model (Millington and Quirk, 1961) was used to predict effective diffusivity of gas through soil due to its simplicity. To implement the prediction of N_2O emissions using DAYCENT submodel in IFSM, seven inputs were needed: soil nitrification rate, soil bulk density, nitrate concentration in each soil layer, CO_2 flux, WFPS, air-filled pore space, and total porosity (Chianese et al., 2009c).

The effect of manure type and application method could be simulated in IFSM. Two types of livestock farms could be simulated: dairy and beef. Within each livestock farm, manure could be managed as liquid-slurry, slurry, semi-solid and solid. Application method options included no incorporation, incorporation within a week, incorporation within two days, and incorporation within the same day. Application rates could be specified based on mass of N per hectare and selection of manure as N source. The type and amount of bedding material could also be specified, along with length of manure storage. Based on the documentation for IFSM (Rotz et al., 2009), manure incorporation affected only the ammonia volatilization and did not influence the denitrification rate in the simulation. By reducing the ammonia volatilization rate, incorporation increased the N available for denitrification, but the anaerobic conditions beneath the soil surface and resulting enhanced denitrification were not accounted for.

Preliminary simulations using IFSM showed that, for solid manure applications, incorporation within same day or 2 days reduced total ammonia lost by 35% compared to no incorporation, but N_2O emissions (total and maximum daily) were unchanged. For liquid manure application, incorporation within same day or two days reduced total ammonia by more than 50% and total N_2O emission increased slightly (less than 10%), likely due to the increased N available for

denitrification. The maximum daily N_2O emission did not change with application method. Other factors such as soil texture had significant effects on the total N_2O emissions with emissions from heavy clay soils being two to three times higher than emissions from loam soils. These results are consistent with the explanation in the documentation; the enhanced denitrification due to subsurface application was not considered a factor in the IFSM model.

6.3.4.6 FarmGHG

Weiske et al. (2006) presented the effect of mitigation options on GHG emissions of dairy farms in Europe using the flow-based simulation model FarmGHG described by Olesen et al. (2004) in Weiske et al. (2006). The model calculated C and N budgets of the whole farm including imports and exports and quantified all direct and indirect gaseous emissions of the farming system. IPCC emission factors were used to calculate direct and indirect N_2O emissions. The GHG reduction measures studied included (but were not limited to) improving the manure application techniques. Specifically, slurry application by trail hose and by injection was compared to broadcasting. Default factors from various literature sources were used to determine the effective applied N (total applied N – volatilized N) and leached N from different application methods.

The results from Weiske et al. (2006) showed that trail hose and injection reduced GHG emissions by 0.7% and 3.2%, respectively, compared to broadcasting, mainly due to lower indirect losses. For trail hose application, the reduction of NH_3 emission reported in the literature amounted to 10-40% and the reduction was up to 90% for injection of slurry (Weiske et al., 2006). The improved application method influenced the fertilizer replacement values of the applied liquid part of FYM and slurries. The effect of improved application techniques were calculated by not only adapting emission factors, but also by changing manure storage time, NH_3 volatilization, and nitrate leaching since the improved N fertilizer replacement value would result in lower application rates. The authors concluded that improved manure application techniques reduced NH_3 volatilization and thus indirect N_2O emissions, resulting in more nitrogen effectively being applied to the soil. This increased nitrate leaching (and subsequent indirect N_2O emissions), increased the amount of nitrogen available for the crop which resulted in an increase in crop yields. However, the authors noted that there was a trade-off between higher yields and higher costs associated with improved manure handling techniques (Weiske et al., 2006). Since

subsurface application resulted in an overall decrease in emissions, the reduction of indirect emissions from lower ammonia volatilization was higher than the increase of indirect emissions from nitrate leaching. However, the enhanced denitrification was not accounted for, so direct N_2O emissions were likely underestimated.

6.4 Discussion

6.4.1 Impact of application method on nitrogen transformations

When assessing N transformations and total N loss from manure spreading, the ammonia (NH_3) volatilization and nitrate (NO_3) movement obviously must be considered. The IPCC methodology suggests that 1% of volatilized N and 0.75% of leached N are considered indirect sources of N_2O-N. The IPCC methodology suggests that 20% of applied manure N will be volatilized, regardless of application method. Although this study did not comprehensively study the ammonia emissions from manure spreading, preliminary unpublished data suggested that subsurface application of solid poultry manure reduced ammonia emissions by 98% immediately after application. The effect of subsurface application on reducing ammonia emissions from slurry has been well documented to be up to 90% (Huijsmans et al., 2001; Weiske et al., 2006), depending on the manure type, weather conditions and application rate. This reduction value is important because reducing ammonia losses increases the amount of N available for plant uptake and microbial transformations like nitrification and denitrification. However, injection of liquid swine manure increases plant N recovery in Saskatchewan soils (Mooleki et al., 2002). If plant uptake of ammonium occurs before the ammonium has a chance to nitrify, N_2O emissions should be reduced accordingly. Subsurface placement may increase the proportion of ammonium added that is assimilated by crop roots, since the ammonium will be closer to the roots. This is another placement aspect that models do not appear to take into consideration. In addition, leaching losses were estimated to be 30% of applied N in the IPCC methodology (Del Grosso et al., 2006). But leaching losses may be affected by application method due to increased effective application rate and placement deeper in the soil profile.

To illustrate the effect of these trade-offs between NH_3 volatilization and direct and indirect emissions of N_2O (as well as the impact of enhanced denitrification), a mass balance of nitrogen after application was estimated. As depicted in Figure 6.4, the input N was assumed to take six possible pathways:

1. Ammonia volatilization (contributing to indirect N_2O)
2. Nitrate runoff (contributing to indirect N_2O)
3. Nitrate leaching (contributing to indirect N_2O)
4. Ammonium and nitrate uptake in plants
5. Organic N retained in soil
6. Nitrification/denitrification (contributing to direct N_2O)

In each category bubble of the outputs depicted in Figure 6.4, the top number represents the actual mass of total N that is lost or retained in that pathway. The bottom number represents the percentage (or proportion) of the total input N that is lost or retained in that pathway. These percentages were derived from selected literature values summarized in Table 6.3. Note that the anticipated range of values would be greater if all sources and conditions surrounding land application of manure were covered.

Table 6.3. Literature values for approximate N mass balance after manure spreading.

Reference	Volatilization	Runoff/Leaching	Plant uptake	Soil retention	Denitrification
Zhou et al. (2009)	2-4%	11-15%	32-39%	2-6%	30-40%
Cameron et al. (1995)	10%	5%	35%	14%	39%
Carey et al. (1997)	15-26%	8-19%	20%	14-18%	30%
Whalen and DeBerardinis (2007)	5-20%		25-117%	5-20%	<2%

Zhou et al. (2009): liquid cattle waste applied to Japanese paddy fields
Cameron et al. (1995): pig effluent applied to stony pasture land in New Zealand
Carey et al. (1997): pig effluent applied to pasture land in New Zealand
Whalen et al. (2007): irrigated liquid swine waste applied to arable land in US

In most studies, the percent lost to denitrification was assumed to be the difference between the amount of N applied and the amount of N recovered in the other pathways. This likely overestimated the loss to denitrification due to system leakage or measurement errors. In some cases, the amount of N lost to a pathway varied due to conditions specific to the study. For

example, the volatilization losses in Zhou et al. (2009) were very low due to application to flooded rice fields. In Whalen et al. (2007), the plant uptake of N exceeded 100%, possibly due to mineralization and nitrification of residual organic N in the soil. Nitrogen losses by processes like leaching are likely to be much different under semi-arid conditions in Western Canada versus humid New Zealand as reported by Carey et al (1997).

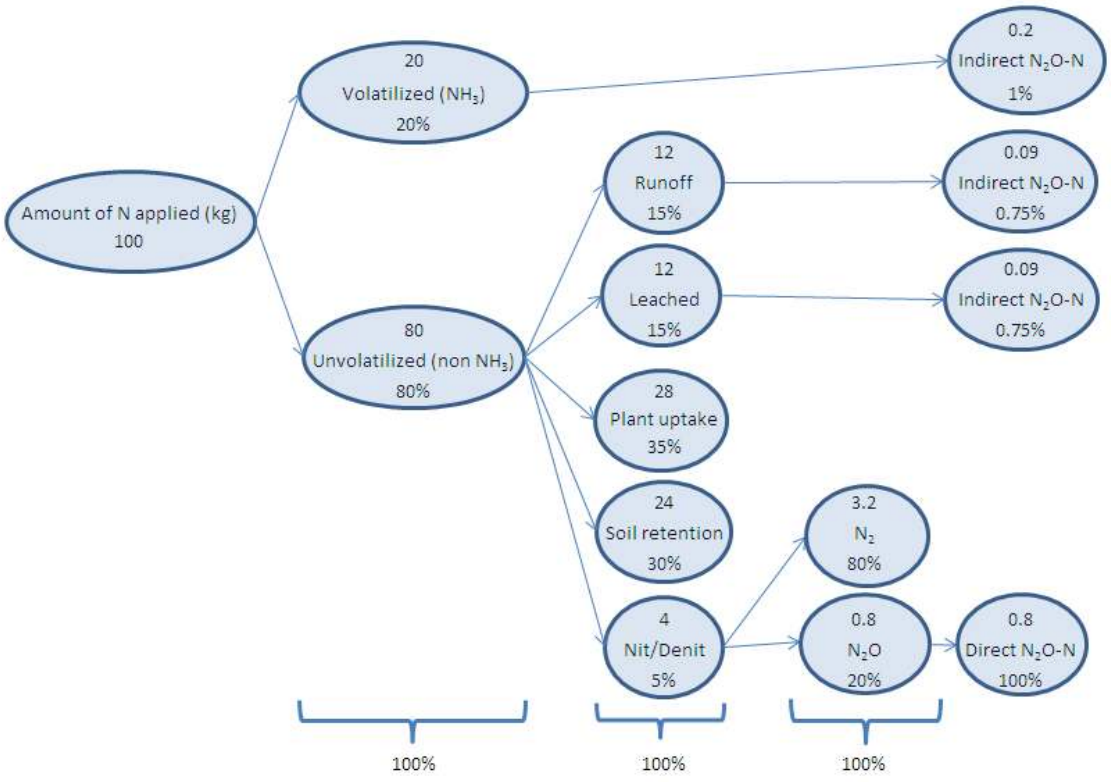


Figure 6.4. Mass balance of nitrogen after manure spreading. Values represent Case 1 conditions.

Other studies reported on the ratio of N_2O:N_2O+N_2 which gives an indication of the degree of incomplete denitrification which results in a net emission of N_2O. Mkhabela et al. (2008) reported the ratio to be between 0.5 and 1.2 while others reported the ratio to be as low as 0.1 to 0.4 (Elmi et al., 2003, Lowrance et al., 1998, Webster and Hopkins, 1996 in: Mkhabela et al., 2008). Incomplete denitrification is thought to be dependent on the carbon to nitrogen ratio and water filled pore space (WFPS). If the carbon content cannot sustain the complete reduction of nitrate to nitrogen gas, the denitrification process will be incomplete and a net emission of N_2O will occur. Also, when the WFPS is between 45 and 75%, both nitrification and denitrification

can occur, increasing the chance of a net N_2O emission since N_2O is a by-product of both processes.

The nitrogen pathways are also known to change with management practices, weather and soil conditions, and application rate. For this illustration, the weather and soil conditions and application rate were assumed to be such that they did not promote excessive losses via runoff/leaching or volatilization. Generally, it is known that subsurface application reduces losses of NH_3 to volatilization, reduces runoff losses of NO_3, increases leaching losses of NO_3, and increases plant uptake. However, the effect of subsurface application on the nitrification/denitrification potential is not well known, but it could significantly impact the estimation of N_2O emissions from manure spreading. The effects of subsurface application and degree of denitrification on total N losses and N_2O emissions were estimated by examining five different cases, outlined in Tables 6.4 and 6.5.

Table 6.4. Illustrative cases to estimate the effects of injection and degree of denitrification on total N losses and N_2O emissions.

Case 1	Surface application (base case)
Case 2	Injection, assuming no enhanced denitrification
Case 3	Injection, assuming enhanced denitrification
Case 4	Injection, assuming enhanced denitrification and limited plant uptake
Case 5	Surface application, assuming limited plant uptake

Table 6.5. Effect of injection and degree of denitrification on N pathways.

		% of unvolatilized that goes to					
Case	% volatilized	runoff	leaching	plant uptake	soil retention	nit/denit	% of denitrified N that is N_2O
1	20	15	15	35	30	5	20
2	5	5	20	40	30	5	20
3	5	5	20	40	25	10	50
4	5	5	25	10	35	25	50
5	20	15	15	10	35	25	20

In Figure 6.4, the fraction that NH_3 and NO_3 contribute to indirect N_2O emissions were assumed to be 1% and 0.75%, respectively, based on IPCC estimates. The fractions of applied N that are lost to each pathway were assumed to vary based on the cases outlined in Table 6.4 and are included in Table 6.5. Figure 6.4 shows the mass balance for Case 1.

For each case, the total N lost was calculated (sum of volatilized N, runoff N, leached N and denitrified N), as well as indirect N_2O-N (sum of indirect N_2O-N from volatilized N, runoff N and leached N) and direct N_2O-N (N_2O-N from denitrification). Those results are summarized in Table 6.6.

Table 6.6. Total N lost and N_2O-N emitted from manure spreading for different management cases for 100 kg applied.

	Case 1	Case 2	Case 3	Case 4	Case 5
Total N lost (kg)	48.00	33.50	38.25	57.25	64.00
Direct N_2O-N (kg)	0.80	0.95	4.75	11.88	4.00
Indirect N_2O-N (kg)	0.38	0.23	0.23	0.26	0.38
Total N_2O-N (kg)	1.18	1.18	4.98	12.14	4.38

The values for case 1 follow the IPCC assumptions that 20% of N will be volatilized as NH_3 and 30% will be lost to runoff/leaching. The IPCC emission factors estimate that total N_2O-N emissions will be between 1 and 1.25% of N applied (between 1 and 1.25 kg in this case). Since total N_2O-N emitted in case 1 is within this range, the percentages estimated in Table 6.5 for case 1 are reasonable.

Based on these results, overall N loss is minimized when manure is injected, provided it is applied when there will be significant plant uptake (cases 2 and 3). The total N_2O-N from case 1 (surface application) is equivalent to case 2 (injected) because the percentage lost to denitrification is assumed to be the same. The indirect N_2O-N is lower in case 2 because of lower NH_3 volatilization, but direct N_2O-N is slightly higher due to a higher fraction of unvolatilized N available for denitrification. Overall N loss is considerably lower in case 2 because of improved plant uptake.

In case 3, injection is assumed to enhance denitrification, so the percent lost to denitrification is increased from 5% to 10%. In addition, the proportion of denitrified N that is emitted as N_2O is increased from 20% to 50% in case 3. Both of these changes are reasonable since injection results in conditions that promote N_2O production through nitrification (increased microbial contact) and denitrification (low oxygen). These changes result in N_2O-N emissions that are more than four times higher than those in case 2. In cases 4 and 5, since there is limited plant

uptake, excess N is available for denitrification. Total N losses and N_2O-N emissions are considerably higher than the base case.

6.4.2 Improved modeling of emissions from manure injection

To better estimate the emission factors used in the above illustration, the ecosystem models described previously need to be modified to account for the important chemical and physical phenomena associated with the fate of applied N and N_2O production after manure injection. This will be site-specific and involve accounting for the enhanced denitrification that occurs after manure injection. This enhanced denitrification is likely due to:

- rapid microbial activity (due to tillage action and close contact between soil and manure) utilizing existing oxygen,
- slow oxygen diffusion into soil, and
- increased and fluctuating WFPS due to slurry application.

These three conditions exist for both surface and subsurface applied manure, but their effects are magnified for subsurface applications. Injected manure has a much higher surface area contact with the microbes in the soil and the diffusion path for oxygen is greater for injected manure than surface applied manure. Because injected manure is applied in narrower bands than surface applied manure, the same volume will have a larger impact on the WFPS for injected manure.

The first two conditions produce partially anaerobic conditions which promote denitrification and N_2O generation. While increasing the WFPS is likely to further reduce air content, the effect of fluctuating WFPS may also result in increased N_2O production. Müller et al. (1997) noted that the highest N_2O emissions were commonly observed under fluctuating moisture conditions. Such conditions promoted varying rates of enzyme production, and highest N_2O emissions were observed during times when the system adjusts to the new situation (Firestone and Tiedge 1979 in: Müller et al., 1997). However, not all microbiological processes in the soil will adjust equally fast to the new conditions, leading to situations where N_2O production rates may be much larger than N_2O reduction rates and therefore resulting in substantially enhanced N_2O emissions (Müller et al., 1997). The effect of injection on WFPS is likely to be short-lived, particularly for

slurry injection. The rapid microbial activity in anaerobic conditions will contribute the most to N_2O emissions after manure injection. For solid manure injection, the minimal movement and slow release of the substrate will likely contribute to elevated emissions for an extended period of time.

In the DNDC model, denitrification is activated when soil water content increases or when soil oxygen availability decreases due to rain, irrigation, or cold temperatures. It is likely that the model does not account for increased soil water content or reduced oxygen diffusion for manure injection. As well, in DNDC, denitrification occurs in the "anaerobic balloon". When subsurface application of manure is simulated, the anaerobic balloon could be expanded. In DAYCENT, denitrification is also highly dependent on WFPS so the effect of manure injection on WFPS needs to be included. The model also needs to account for the changes in microbial community structure due to injection on denitrification rates. Another aspect of manure injection that must be accounted for in these models is the greater retention of N in the soil and the better ability of crop roots to access and take up the manure N before it undergoes nitrification. Subsurface application will place the ammonium closer to the roots, increasing availability and potential plant uptake, reducing the potential for denitrification during the growing season.

For the simplified process models that use Michaelis-Menten kinetics to describe cumulative N_2O emissions, the model parameters (N_{max}, K_m) that describe the maximum emission and time at which the emission rate is half of the maximum would theoretically be dependent on application method. However, an ammonia loss calculator developed by Alberta Agriculture and Rural Development (Guoliang Qu, personal communication) assumed that the K_m value in the Michaelis-Menten function for cumulative ammonia emission was not dependent on application mode (broadcast, banding, sleighfoot, shallow injection, deep injection). The maximum value (N_{max}) was dependent on application method. Both parameters (N_{max} and K_m) were dependent on other variables such as soil moisture, air temperature, wind speed, dry matter content of manure, total ammoniacal N in manure, and application rate. However, ammonia emissions are driven primarily by volatilization and are not dependent on microbial processes like nitrification and denitrification. The complex interactions that drive N_2O emissions after manure spreading mean that both Michaelis-Menten parameters could be affected by method of application.

Unfortunately, the only way to determine these parameters is empirically by analyzing available data, or by collecting specific data under controlled conditions.

6.5 Conclusions

Agricultural management practices can have a large impact on the net emission of greenhouse gases, particularly N_2O from application of N fertilizer and manure. Previous work showed that application method influenced short-term direct emissions while a simple follow-up study showed that application method also affects longer-term direct emissions. The nutrient transformations that drive N_2O production and the effects of soil and environmental conditions that dictate diffusion and emission are very complex. Therefore, a comprehensive whole-farm evaluation is needed, which can be achieved through simulation models. Existing methodologies and models either do not include manure application method as a management practice or they do not account for the changes in the physical and chemical soil environment caused by manure injection. These omissions result in uncertainties in estimation of N_2O emissions from manure spreading, particularly manure injection. In most models, denitrification is governed by oxygen content and water filled pore space. By incorporating the effects of manure application on these parameters, as well as the enhanced microbial activity due to intimate contact between the manure and soil, the effect of application method on long-term direct and indirect emissions can be simulated. This will allow the improved estimation of the economic and environmental impacts of manure injection, which can be incorporated into decision support systems for agricultural GHG mitigation.

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Chapter 7

7.0 General Summary and Discussion

The general summary and recommendations of this thesis are presented here, starting with a review of the project objectives, a summary of chapter two to chapter six, and a list of general conclusions.

7.1 Summary of Thesis

Land application of livestock manure is a very common practice that can potentially impact soil, water, and air quality surrounding the application site. Very little data exist on the impacts of manure type and application method on odour and greenhouse gas emissions. Therefore, the objectives of this work included:

- evaluating existing equipment and protocols for emission determination following land application of manure and, if required, developing new protocols and equipment for sample collection (Chapter 3 for odour and Chapter 4 for greenhouse gas emissions),
- evaluating the relative odour and GHG emissions from various types of solid and liquid manure following surface and sub-surface application (Chapter 3 for odour and Chapter 4 for greenhouse gas emissions),
- developing and validating a mechanistic model for the prediction of the odour emission rate following land application of liquid and solid manure (Chapter 5), and
- reviewing the suitability of existing GHG emission models for the prediction of emissions following surface and subsurface application of manure (Chapter 6).

As discussed in Chapter 2, organic fertilizers like livestock manure have several benefits over synthetic fertilizers, including increasing the organic matter content and microbial activity in the soil and maintaining the soil's ability to recycle nutrients. However, over-application or improper timing of manure application can result in contamination of the soil and water or excessive atmospheric emissions. The nutrients in manure and soil are transformed via microbial processes such as mineralization, nitrification and denitrification. Specific forms of nitrogen such as nitrate and ammonia are more susceptible to leaching or volatilization, increasing the risk of environmental contamination. Nitrate nitrogen can pollute surface and groundwater, posing a human health risk, ammonia emissions lower the N availability to crops, while nitrous oxide and methane contribute to the greenhouse gas effect. Balancing the N loss dynamics from fertilized soil is very difficult because the nutrient transformations are affected by the soil environment such as air and water content, pH, and labile carbon content. All of these soil environmental factors can be influenced by manure application practices such as application rate, timing and manure placement. Knowledge of how these management practices affect the soil environment can help producers make management decisions that reduce the likelihood of soil, water and air contamination from manure application.

In addition to specific environmental risks, manure spreading also results in odour emissions. Odours from manure application activities can hinder the expansion of the livestock industry because of the potential nuisance to neighbours. Chapter 3 investigated the effects of management practices such as application mode and application rate on odour emissions from both solid and liquid manure spreading. First, sampling methods and protocols for assessing odour emissions from manure spreading were established. Dynamic flux chambers were used in this study for surface odour emission measurement. Based on the results of an experiment with a simulated carbon dioxide flux, a sweep air flow rate of 0.944 L/s was used in the chamber. It was noted that the optimal sweep air flow rate depended on the magnitude of the measured emissions. It was recommended to obtain baseline odour emission data to better select an appropriate sweep air flow rate.

Odour emission data were collected immediately after application of five livestock manure species applied at three application rates using surface and subsurface application methods. The

results of the study indicated that odour concentrations from injected plots were up to 66% (37% on average) lower than concentrations from broadcasted applications. Injection seemed to have a larger impact on reducing odours from solid manure than liquid manure, mainly due to better manure coverage from solid manure injection. Odours from solid manure applications were also 37% lower than from liquid manure applications. In general, odours from liquid and solid manure increased with higher application rates, but there was little difference among one, two and three year application rates. The specific odour rate decreased with higher application rates due to the reduced surface area available for volatilization of compounds with higher application rates. Higher application rates did result in higher overall odour concentrations, but this increase was not proportional to the amount of N applied.

While the effects of manure type, application method, and application rate on odour emissions measured one time after application were discussed in Chapter 3, the odour emission rate trend over the first 48 hours after application was modeled in Chapter 5. The emission rate trend over time after application is essential for the application of dispersion models to optimize the minimum separation distances for manure spreading activities. The model parameters for an existing volatilization model were determined from field and literature data and the resulting model allowed the effects of application mode (surface vs. subsurface) and manure type (liquid vs. solid) on odour emissions to be simulated. The effects of injection depth and a coverage factor on emissions were also simulated.

The modeled peak fluxes from liquid manure applications were higher than those for solid manure applications, but the extended duration of odour emissions for solid manure resulted in higher cumulative losses from solid manure applications. While the application rate had no effect on the initial odour flux, higher application rates resulted in higher peak fluxes, higher overall emissions, and longer odour durations for both manure types and application methods. When typical coverage factors were assumed, the reductions in cumulative odours due to injection were approximately 75, 55, and 30% for liquid manure at 1X, 2X, and 3X application rates, respectively and 90, 80, and 70% for solid manure. Injection depths as low as 0.05 m were shown to significantly reduce odours from both liquid and solid manure applications compared to surface spreading.

Based on the results obtained in Chapters 3 and 5 of this thesis, injection or subsurface application of manure was identified as an effective way to reduce odour emissions from manure application, particularly for solid manure. However, placing the manure under the soil surface has the potential to increase greenhouse gas (GHG) emissions due to enhanced microbial activity. Therefore, the impact of manure type and application method on GHG emissions from manure spreading was investigated in Chapter 4. For this initial comparison, all measurements were made 24 hours after application. Samples were collected using the static chamber technique and the samples were analyzed using gas chromatography.

The GHG results in Chapter 4 showed that subsurface application significantly increased carbon dioxide equivalent (CO_2-e) fluxes for both solid and liquid manure. The overall CO_2-e fluxes from the injected treatments were 3.2 times higher than CO_2-e fluxes from the surface applied plots. This was explained by the creation of conditions, particularly with liquid injection, that were highly conducive to the conversion of the available N and C to GHG, especially N to N_2O and N_2 by denitrification. The CO_2-e fluxes from the liquid manure applications were also higher than the CO_2-e fluxes from the solid manure applications, probably due to higher levels of ammonium available for nitrification and subsequent denitrification. The CH_4 fluxes were generally low and the treatments had no effect in this study. For this particular study, the measured specific fluxes (total flux per kg N applied) remained relatively constant with application rate, indicating that GHG emissions from manure applications were approximately proportional to the amount of manure applied to the land.

It was stressed that these comparisons were only valid for the first 24 hrs following land application. Manure type and application method have the potential to impact long term GHG emissions. For example, solid manure generally has a higher C content, which will mineralize slowly over time, likely providing for sustained denitrification if the conditions remain anaerobic. It is likely that conditions beneath the soil surface will remain anaerobic for long periods of time as the diffusion rate of oxygen into the topsoil is often lower than the rate of oxygen use by the increased microbial activity. This could result in the total emissions from solid manure application being higher than total emissions from liquid manure application. In Chapter 6, application method was shown to influence longer-term emissions. The seven day cumulative

nitrous oxide emissions were 22 times higher from the injected solid manure than the surface applied solid manure.

Because of those results, the ability of existing GHG emission models to predict the long term emissions following surface and subsurface application of manure was assessed in Chapter 6. Numerous process based models exist for the estimation of regional and national GHG inventories, ranging from simplified process models and methodologies to complex ecosystem models. However, most models do not account for application method and those that do include an application mode do not account for enhanced denitrification that exists after slurry injection or manure incorporation. If the results from the seven day study are any indication, the omission of enhanced denitrification in the models could potentially result in a significant underestimation of N_2O emissions from manure spreading.

In most models, denitrification is governed by oxygen content and water filled pore space. By incorporating the effects of manure application on these parameters, as well as the enhanced microbial activity due to intimate contact between the manure and soil, the effect of application method on long-term direct and indirect emissions can be better simulated. Modifications to these models will allow the improved estimation of the economic and environmental impacts of manure injection, which can be incorporated into decision support systems for agricultural GHG mitigation.

7.2 General Conclusions

The general conclusions of this study are summarized here:

1. Vented flux chambers and dynamic dilution olfactometry are well suited for comparing odour emissions among several field treatments. A sweep airflow rate in the flux chamber of 0.944 L/s worked well for the magnitude of emissions in this study. Proper selection of the sweep airflow rate prevents sample dilution and suppression of emissions from the surface.
2. Subsurface application of manure significantly reduced odour emissions measured immediately after application of both solid and liquid manure. Subsurface application

appeared to reduce odours more efficiently for solid manure, mainly due to improved soil coverage at the higher application rates.

3. Liquid manure generated significantly higher odour emissions than solid manure immediately after application.
4. Odour emissions increased with application rate, but there was no significant difference among the one-, two-, and three-year application rates.
5. Specific odour emissions (OU $(kg\ N)^{-1}\ s^{-1}$) actually decreased with application rate. This was likely due to reduced contact area between manure and air (resulting in less volatilization) at higher application rates.
6. The odour model results showed that liquid manure applications resulted in a higher peak flux than solid manure applications, but cumulative odour emissions (over 48 hours) were higher from solid manure applications. This is due to the higher degradation rate of odour in liquid manure and the infiltration of liquid manure into the topsoil.
7. The odour model results showed that injection reduced overall emissions for both manure types and all application rates, even when reasonable coverage factors were assumed. Modest injection depths were also shown to significantly reduce odours compared to surface applications.
8. The static chamber technique was well suited for comparing greenhouse gas fluxes among several treatments. Because soil fluxes in the Canadian Prairies are relatively low, the rate of increase in gas concentration in the chamber headspace was best represented by linear (and occasionally quadratic) regression models.
9. Subsurface application significantly increased nitrous oxide and carbon dioxide equivalent fluxes measured 24 hours after application. This was because the conditions beneath the surface enhanced denitrification activity.
10. Greenhouse gas emissions from liquid manure applications were significantly higher than emissions from solid manure applications measured 24 hours after application.
11. Greenhouse gas emissions measured 24 hours after application increased with application rate, but there was no difference among one-, two-, and three-year application rates. The increase in greenhouse gas emissions with application rate were approximately proportional to the amount of nitrogen applied.

12. Subsurface application increased longer-term (7 day) greenhouse gas emissions, particularly nitrous oxide from solid manure injection.
13. Existing methodologies and process-based models for estimating greenhouse gas emissions do not account for the enhanced denitrification that occurs after subsurface application of manure. Model modifications that account for the effect of manure injection on water filled pore space, microbial respiration, and denitrification activity may improve the ability of models to estimate the impact of application method on overall greenhouse gas emissions.

7.3 General Discussion and Recommendations for Future Work

Manure management decision support systems can be valuable tools for livestock producers, allowing them to analyze the economic and environmental implications of different manure management strategies. Most decision support systems consider the collection, handling, and storage requirements of different manure types (liquid, semi-solid, and solid), as well as the nutrient value of the manure and the energy/cost associated with land application of the manure. Many of these decision support systems also include estimates of emission factors for ammonia, odour and greenhouse gases from the buildings, storages, and land spreading activities. However, there are very few data on the effects of different management strategies (e.g.: subsurface application of solid manure) on these emissions. The information presented in this thesis may influence decisions regarding subsurface application of manure.

When deciding whether or not to inject manure, producers must evaluate the overall environmental and economic impact of the technology. On one hand, subsurface application of livestock manure often constitutes an effective means to reduce odour emissions. However, the need to limit odour complaints must be weighed against the potential economic and environmental costs associated with increased GHG emissions. Since it appears that subsurface application of both solid and liquid manure will increase total GHG emissions over a period of time after application, it may not be possible to reduce both odour and GHG emissions using that

particular management practice. If manure must be injected due to odour or other concerns, nitrous oxide emissions may be limited by adopting management practices that limit nutrient loss such as matching the application rate to the soil and plant requirements and applying when nutrient uptake is highest. Since denitrification is highly dependent on water filled pore space, nitrate content, and labile carbon content, manure should not be injected into wet soils, the use of nitrification inhibitors to limit N_2O emissions should be investigated, and manure with high carbon (bedding) content should not be injected.

In addition to elevated GHG emissions, other environmental and economic issues related to subsurface manure application, such as increased soil compaction, increased energy requirements, soil disturbance, and the increased field area required to dispose of the manure at agronomic rates, must also be considered when assessing the overall impacts of manure injection compared to surface application. Also, the ability of subsurface application to reduce ammonia loss to the air and increase overall plant nitrogen recovery must be considered. The ammonia emissions will potentially contribute to greenhouse gas production somewhere in the terrestrial environment when the nitrogen re-enters the system. These "whole farm and ecosystem assessments" can be made easier by well designed decision support systems.

Odour dispersion modeling is another tool that is often used to help design or site livestock facilities to minimize the odour nuisance to neighbours. Dispersion modeling can be used to establish minimum separation distances between neighbours and buildings and storages. However, the majority of odour complaints are due to manure spreading activities. Dispersion modeling cannot be easily applied to manure spreading because the source emission rate needs to be known for the entire modeling period. Manure type, application rate, and application method are likely to affect this emission rate trend. Therefore, a preliminary model was developed to predict the odour emission rate trend over time after application. The model simulated emissions over 48 hours and was based on manure type, application method, application rate, injection depth, and coverage factor (for subsurface applications). The modelled trends for odour flux variation over time after application and cumulative odour emissions mimicked those found in literature. The percent reductions in odour emissions due to injection calculated from the model also agreed with percent reduction values found in literature. A sensitivity analysis showed that

of the model parameters, effective diffusivity and odour degradation rate influenced the model results the most. Therefore, future work should focus on better estimation of how manure type and application method influence odour degradation rate, and more precise calculation of the variation of effective diffusivity with time and soil conditions. In addition, the effect of weather factors such as temperature fluctuation and rainfall infiltration into the topsoil need to be incorporated into the model to improve the accuracy of the simulated results.

With the potential for carbon credit revenue for farmers, greenhouse gas emission models will become important tools for calculating carbon emissions and credits. However, most of these models are not sensitive enough to assess the effects of different manure management strategies on total greenhouse gas emissions. Unlike odour emissions, greenhouse gas emissions are governed by complex microbial and environmental factors which can influence short- and long-term direct and indirect emissions. Robust and reliable baseline data are required to assess the total impact of manure injection on long-term greenhouse gas emissions. This data can be used to validate the suggested modifications to the models. These models can then be used to assess the relative decrease or increase in emissions due to different management practices. The modified models could also be used to provide better estimates of regional and national greenhouse gas emissions from the agriculture industry.

Emissions from manure spreading constitute a large portion of total livestock emissions. With new plans and strategies being put in place to reduce global greenhouse gas emissions, it is important to carefully analyze emissions that result from new technologies or practices. If the greenhouse gas and odour emissions and dispersion surrounding application sites can be reliably predicted, better decisions can be made so as to not cause nuisance to neighbours while maximizing land-use efficiency and lowering the livestock industry's contribution to agricultural GHG emissions. These decisions require better understanding of the factors that affect odour and greenhouse gas emissions. The information presented in this thesis provides a baseline with which to start making better manure management decisions.